

- ISOMERISM
- ALKYL HALIDE
- GRIGNARD REAGENT

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THEORY AND EXERCISE BOOKLET

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JEE SYLLABUS

- **ISOMERISM**

JEE - ADVANCED

Structural and geometrical isomerism; Optical isomerism of compounds containing up to two asymmetric centres, (R,S and E,Z nomenclature excluded); Conformations of ethane and butane (Newman projections);

- **ALKYL HALIDE**

JEE - ADVANCED

Characteristic reactions of the following (including those mentioned above):Alkyl halides: rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions

- **GRIGNARD REAGENT**

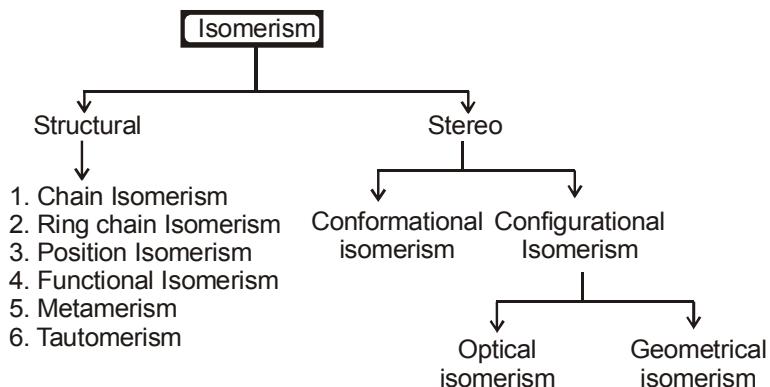
JEE - ADVANCED

Grignard reagent; acid base reactions and nucleophilic substitution reactions.

ISOMERISM

DEFINITION : Compounds having same molecular formula (M.F.) but differ in their properties are known as **isomers** and this phenomenon is known as **isomerism**.

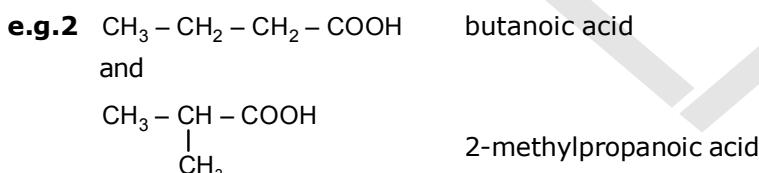
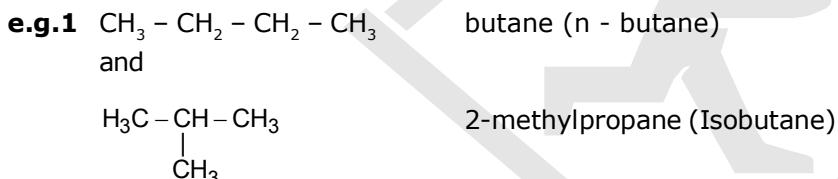
CLASSIFICATION :



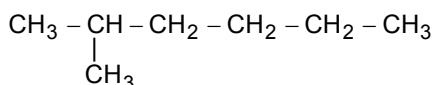
STRUCTURAL ISOMERISM : Compounds having same M.F. and different in connectivity of atom (Structure is different)

CHAIN ISOMERISM

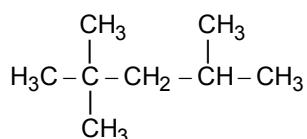
Compounds having same molecular formula but differing in the length of the principal chain.



e.g. Isoheptane

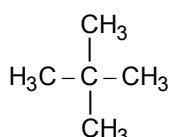


* Isooctane (exception of Iso group)

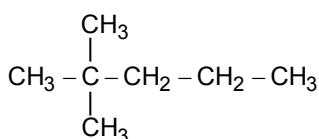


* Neo group $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C} - \text{C} - \\ | \\ \text{CH}_3 \end{array}$

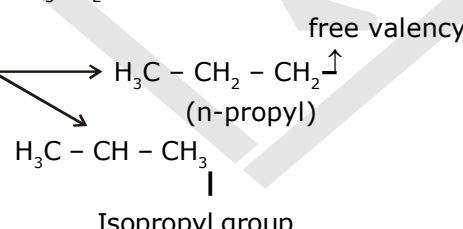
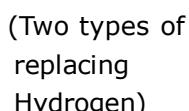
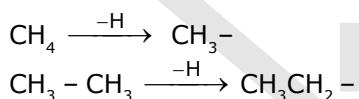
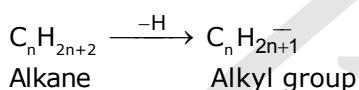
- * To prepare the neo compound firstly the above group ($\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{|}{\text{C}}}-$) is written. After that required no. of carbon is added in the straight chain.
e.g. neopentane



neoheptane

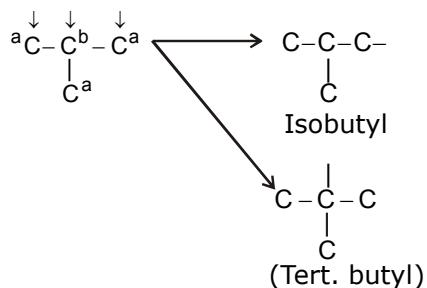
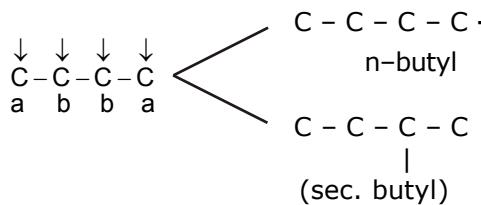


Alkyl Group :



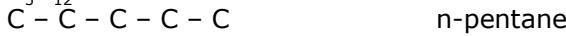
dark line (—) represents vacant valency where any group can be attached.

- * $\begin{array}{c} \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$
 (Iso propyl alcohol)
 Thus we can conclude that
 $\text{C}_3\text{H}_7 - \rightarrow$ Two forms.
 *

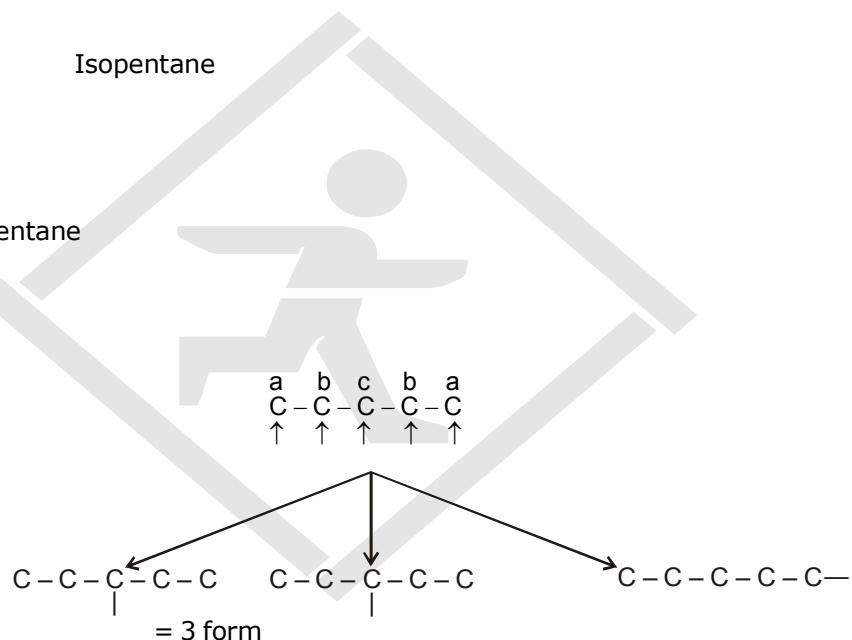


* C_4H_9 = 4 forms.

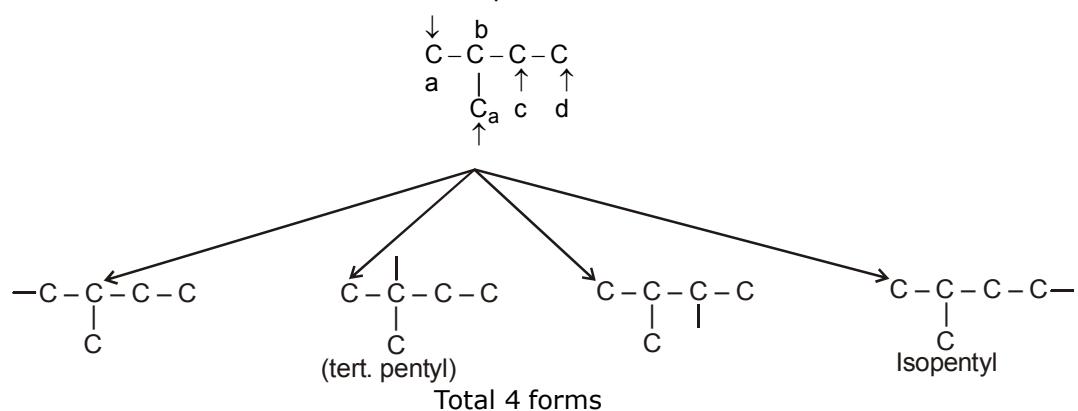
* C_5H_{12} has it's three forms



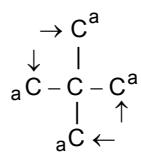
* Consider n-pentane



Consider Isopentan



Consider neopentane



= only one form.

Total forms of C_5H_{11} - = 8

Ex.1 Find all the structural isomers of C_6H_{14}

Sol. C - C - C - C - C - C C-C-C-C-C-C C-C-C-C-C C-C-C-C-C-C C-C-C-C-C

$\begin{array}{c} \text{C} \\ | \\ \text{C} \end{array}$
 $\begin{array}{c} \text{C} \\ | \\ \text{C} \end{array}$
 $\begin{array}{c} \text{C} \\ | \\ \text{C} \end{array}$

POSITION ISOMERISM

Compound having same molecular formula and same principal chain but differ in position of functional group, multiple bond and substitution group are known as position isomers.

e.g. $\text{C} - \text{C} - \text{C} = \text{C}$ and $\text{C} - \text{C} = \text{C} - \text{C}$
 1-butene 2-butene

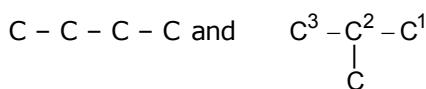
e.g. $\text{C}-\text{C}-\text{C}-\text{Cl}$ and $\text{C}=\text{C}-\text{C}\text{Cl}$ are position isomers

1-chloropropane 2-chloropropane

e.g.	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$ and	$\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{CH}}} - \text{CH}_3$
	1-propanol	2-propanol

*  and  are chain isomer, not position isomer.

The above example can be best understood taking the following example



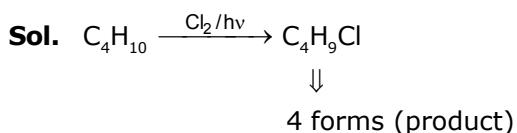
In this the last carbon has been placed to IInd position to form chain isomer the same has happier with above example and hence they are chain isomer to each other.

Ex.2 Find the relation between the given compounds

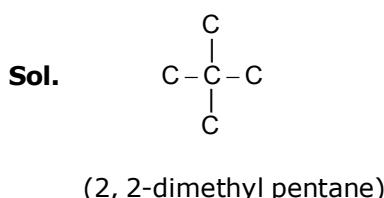
Sol. a, b → chain isomers.
c, d → chain isomers.
b, c → position isomers.
d, e → position isomers.

* Monochlorination → Replace one H by Cl

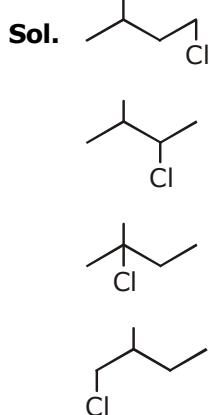
Ex.3 How many monochloro derivative will be of C_4H_{10} (Only structural)



Ex.4 An alkane having molecular formula C_5H_{12} can give only one product on monochlorination. Find the IUPAC name of the alkane

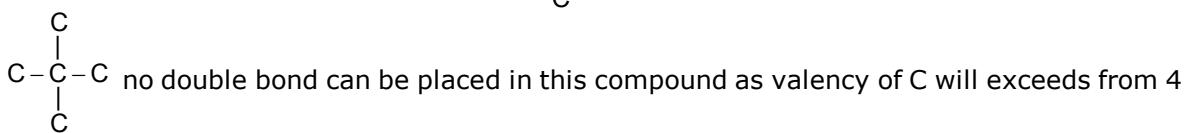


Ex.5 $\xrightarrow{Cl_2/h\nu}$ **Mono chlorinated products (Excluding Stereoisomers)?**



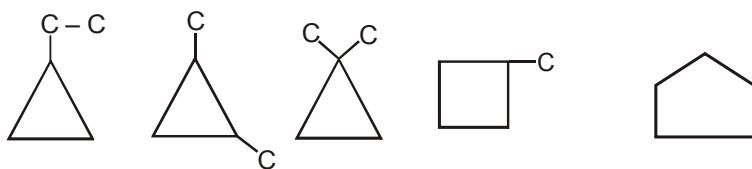
Ex.6 Find the total structural isomer of C_5H_{10} .

Sol. For solving these kinds of problem we should at once draw all possible structure of corresponding alkane and then we should check how many possibilities are there to put double bond.



Total open chain structural isomers = 5

- To form cyclic structural we should always start with 3 carbon ring.

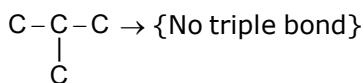
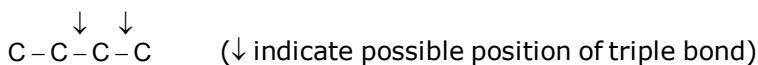


$$\text{total structural isomers} = 5 + 5 = 10$$

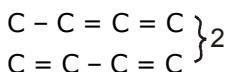
Ex.7 Find the total structural isomers of C_4H_6 .

Sol. Total unsaturation of $C_4H_6 = 2$

i.e. possibility = one triple bond, or 2 double bond or (one ring + one double bond)



for alkene,



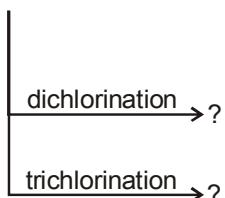
$$\text{total open chain} = 2 + 2 = 4$$

for cyclic

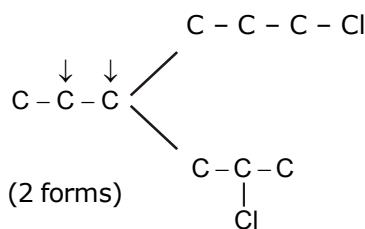


$$\text{total structural isomers (cyclic + acyclic)} = 9$$

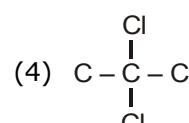
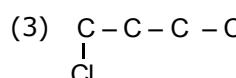
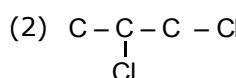
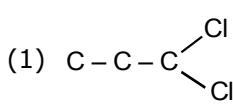
Ex.8 $C_3H_8 \xrightarrow[\text{mono chlorination}]{?} ?$ (Only structural in all)



Sol. For monochloroderivative,

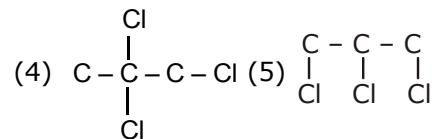
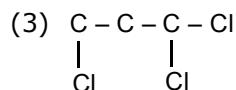
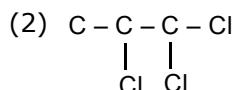
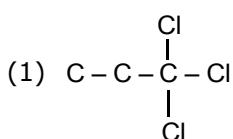


di-chloroderivative



Total dichloroderivative = 4

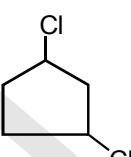
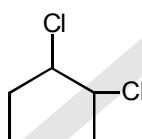
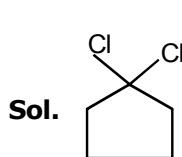
Trichloroderivative,



- * To find di or trichloroderivative

We place two or three chlorine at last carbon and after that rotate one Cl by keeping the other two at the same the place.

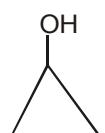
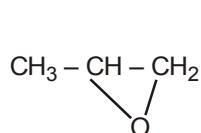
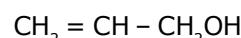
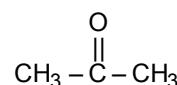
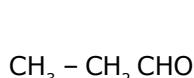
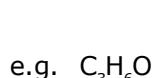
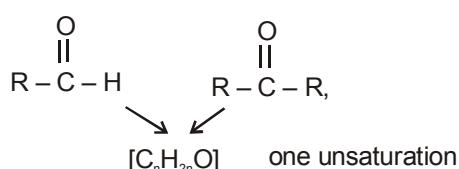
Ex.9 Find all the structural dichloroderivative of cyclopentane.



Total structural isomer = 3

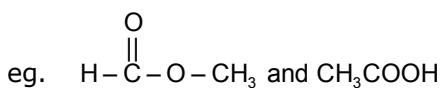
FUNCTIONAL ISOMERISM

Compound having same molecular formula but different in functional group are known as functional isomers.



- * Aldehyde, Ketone, cyclic ethers, cyclic alcohol, unsaturated alcohol etc are functional isomers to each other.

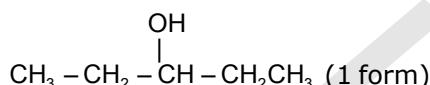
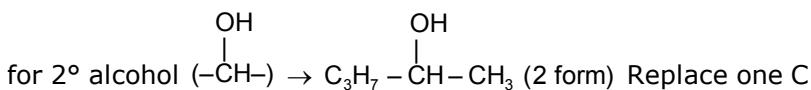
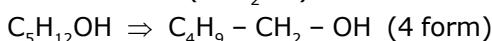
- * Alcohol and ether functional isomers to each other.
e.g. $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3
- * Acids and ester are functional isomers to each other.



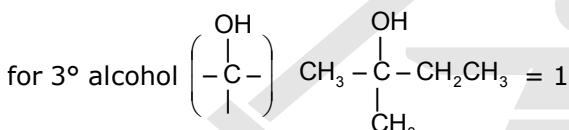
- * Cyanide and Isocyanide are functional isomer to each other but HCN and HNC are tautomers to each other.
- * 1° , 2° and 3° amine are functional isomer to each other.

Ex.10 How many primary, secondary and tertiary alcohol are possible for $\text{C}_5\text{H}_{13}\text{O}$? (Only structural)

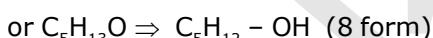
Sol. For 1° alcohol ($-\text{CH}_2\text{OH}$)



total = 3



total = $4 + 3 + 1 = 8$



Ex.11 How many ethers are possible in $\text{C}_5\text{H}_{12}\text{O}$. (Only structural).

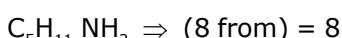
Sol. $\text{C}_4\text{H}_9\text{OCH}_3 \Rightarrow \text{C}_3\text{H}_7\text{OC}_2\text{H}_5$

(4 form) (2 form)

total = 6

Ex.12 How many 1° , 2° and 3° amine are possible for $\text{C}_5\text{H}_{13}\text{N}$ (Only structural).

Sol. For 1° amine ($-\text{NH}_2$)

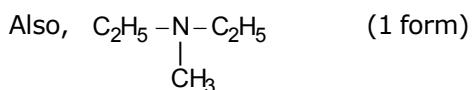


(2 form)

total form at $2^\circ = 4 + 2 = 6$

for 3°

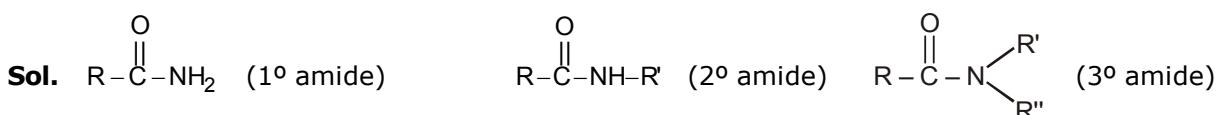




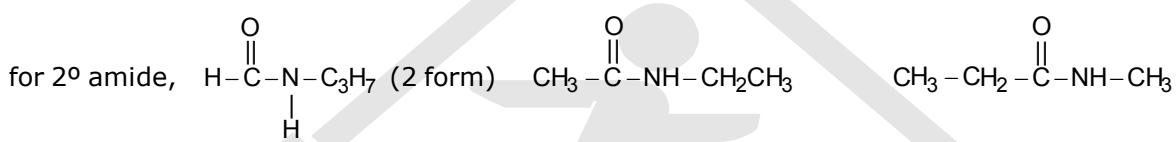
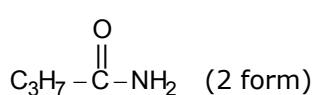
Total form of 3° = 2 + 1 = 3

Total no. of amines = 8 + 6 + 3 = 17

Ex.13 For molecular formula $\text{C}_4\text{H}_9\text{NO}$, how many amide will be there which will not form H-bond ?(Only structural)

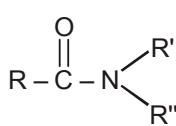


for 1° amide



total 2° amide = 4

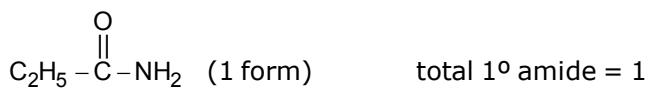
for 3° amide



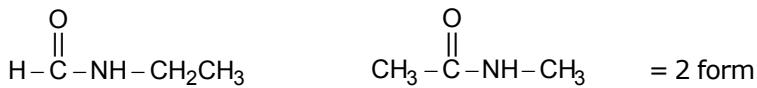
3° amide will not form H-bond hence there will be 2 amides which will not form H-bond.

Ex.14 Find all 1° , 2° and 3° amides for $\text{C}_3\text{H}_7\text{NO}$ (Only structural)

Sol. For 1° amides



for 2° amide



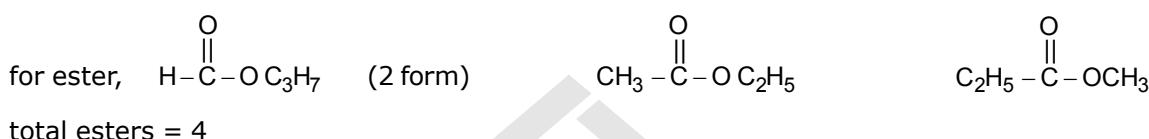
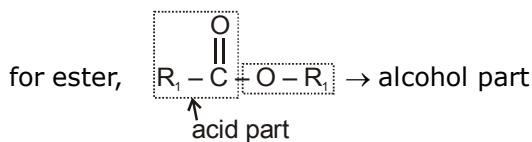
for 3° amide



total amides ($1^\circ + 2^\circ + 3^\circ$) = $1 + 2 + 1 = 4$

Ex.15 Find the total no. of acid and esters from $\text{C}_4\text{H}_8\text{O}_2$ (Only structural)

Sol. For acid, $(-\text{COOH})$ $\text{C}_3\text{H}_7 - \text{COOH}$ (2 form)



Ex.16 $\text{C}_4\text{H}_4\text{O}_4$ may be (Only structural)

(i) Saturated dicarboxylic acid

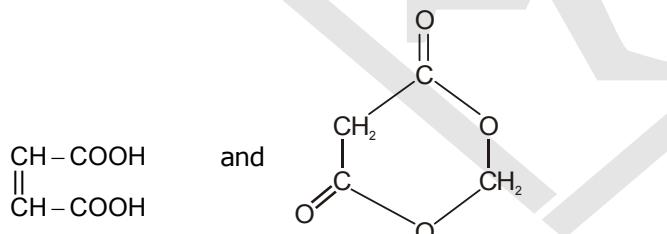
(iii) Cyclic diester

(ii) Unsaturated dicarboxylic acid

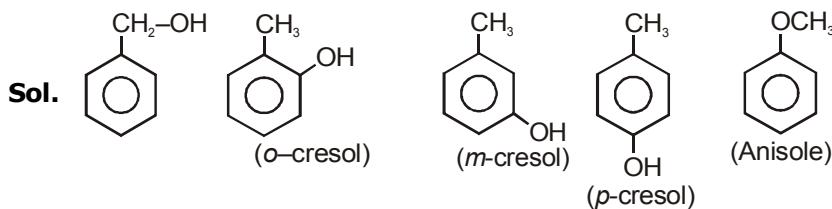
(iv) Saturated di aldehyde

Sol. Three unsaturation.

(ii) and (iii) is the Ans.

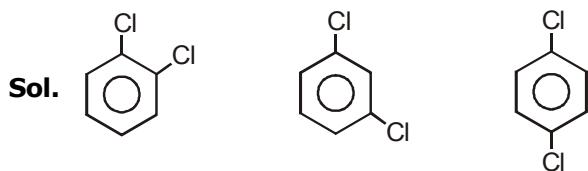


Ex.17 How many aromatic isomers will be possible for $\text{C}_7\text{H}_8\text{O}$ (Only structural)

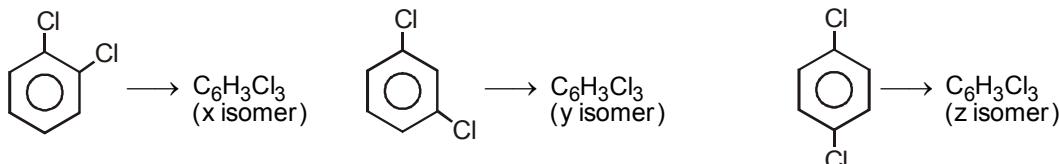


Total = 5

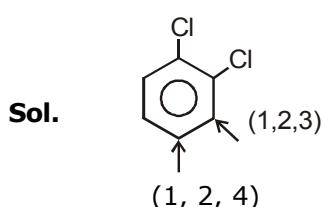
Ex.18 Find the possible dichloroderivative of $\text{C}_6\text{H}_4\text{Cl}_2$ (Only structural)



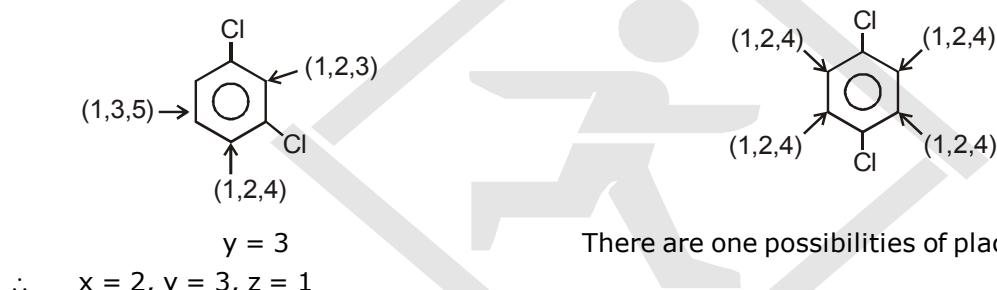
Ex.19 $C_6H_4Cl_2 \rightarrow C_6H_3Cl_3$ (Only structural)



find the value of x, y, z



There are two possibilities placing Cl in place of H.



There are one possibilities of placing Cl, therefore $z = 1$

$$\therefore x = 2, y = 3, z = 1$$

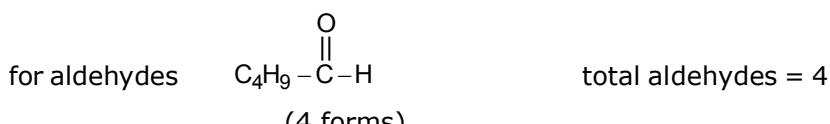
Ex.20 Find the total carbonyl compound (aldehydes and ketones) formed by $C_5H_{10}O$ and also find the relation between carbonyl compounds which have same no. of α -hydrogen.(Only structural)

Sol. For ketones,

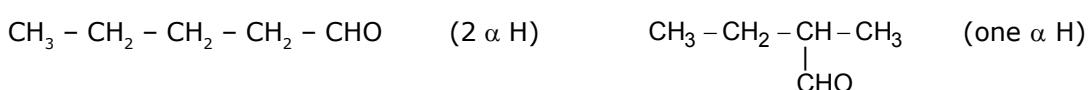


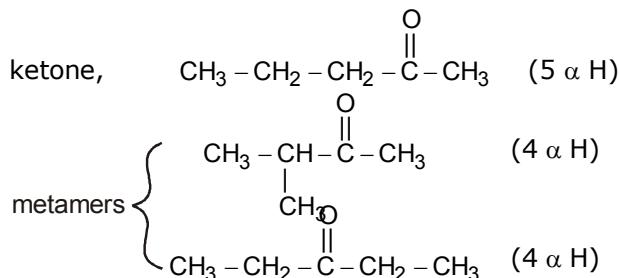
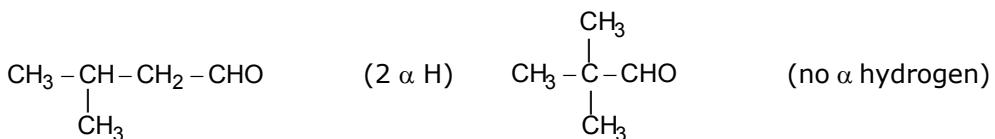
(2 form)

$$\text{total ketones} = 3$$

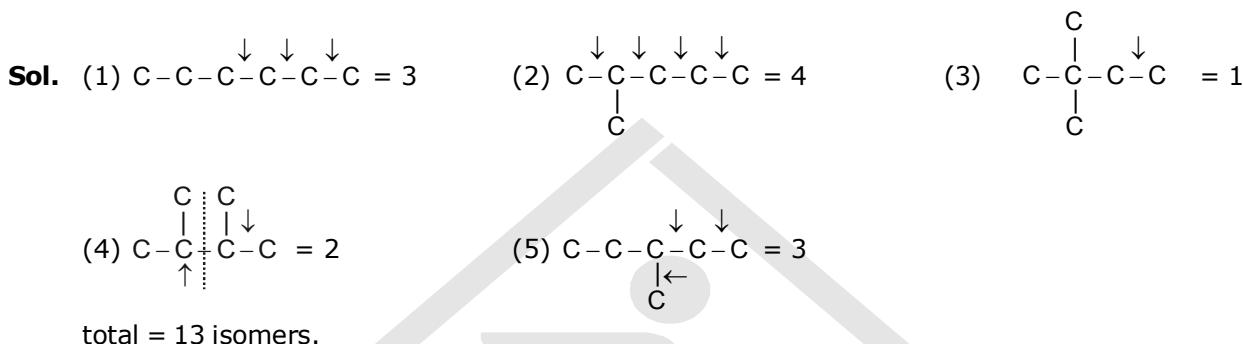


$$\text{total carbonyl compounds} = 4 + 3 = 7$$

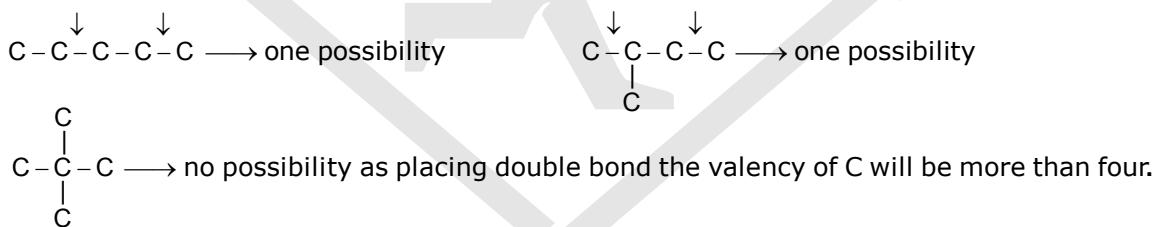




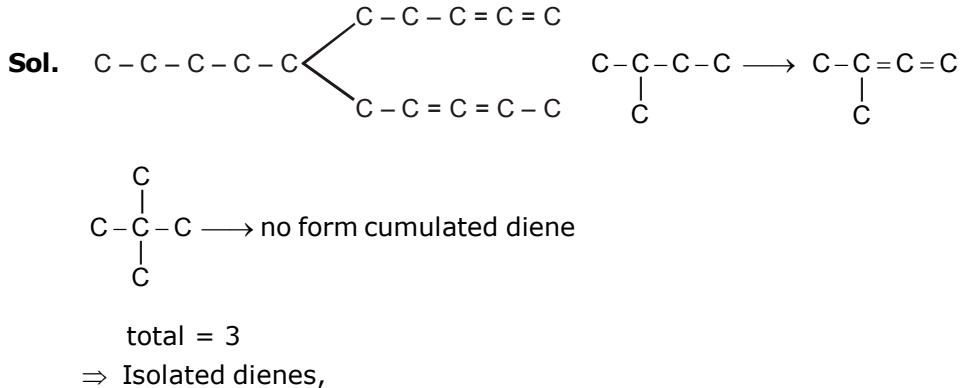
Ex.21 Find total acyclic structural isomer of C_6H_{12} (Only structural)

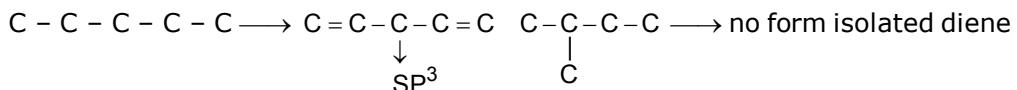


Ex.22 Find the total conjugated diene in C_5H_8 (Only structural)



Ex.23 Find total cumulated diene in C_5H_8 (Only structural)



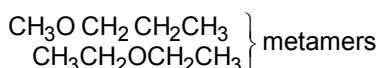


total = 1

METAMERISM

This type of isomerism is found in those types of compounds which have polyvalent atoms or polyvalent functional group, e.g. ether, 2^{o} amine, ester etc.

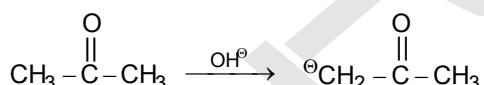
Compound having same molecular formula but differ form the nature of alkyl group directly attached with polyvalent atom or polyvalent functional group



a & b are metamers

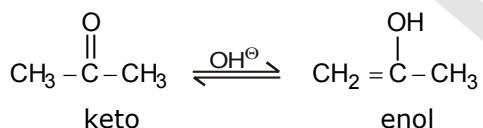
TAUTOMERISM

Compound having same molecular formula but different due to oscillation of an atom (usually H⁺) are known as tautomers.

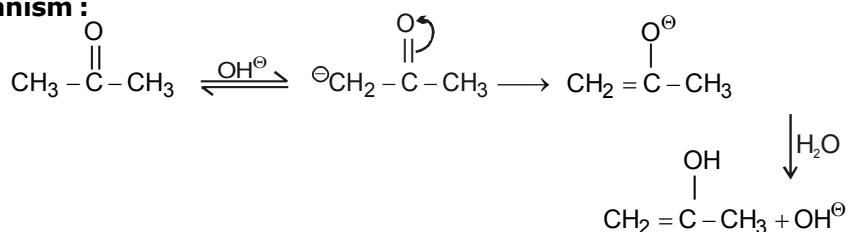


as after removal of H^+ , the anion formed is resonance stabilised.

KETO ENOL TAUTOMERISM



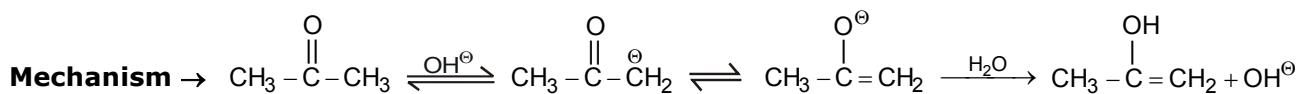
Mechanism :



* OH^{\ominus} acts as catalyst.

Base Catalysed Tautomerism :



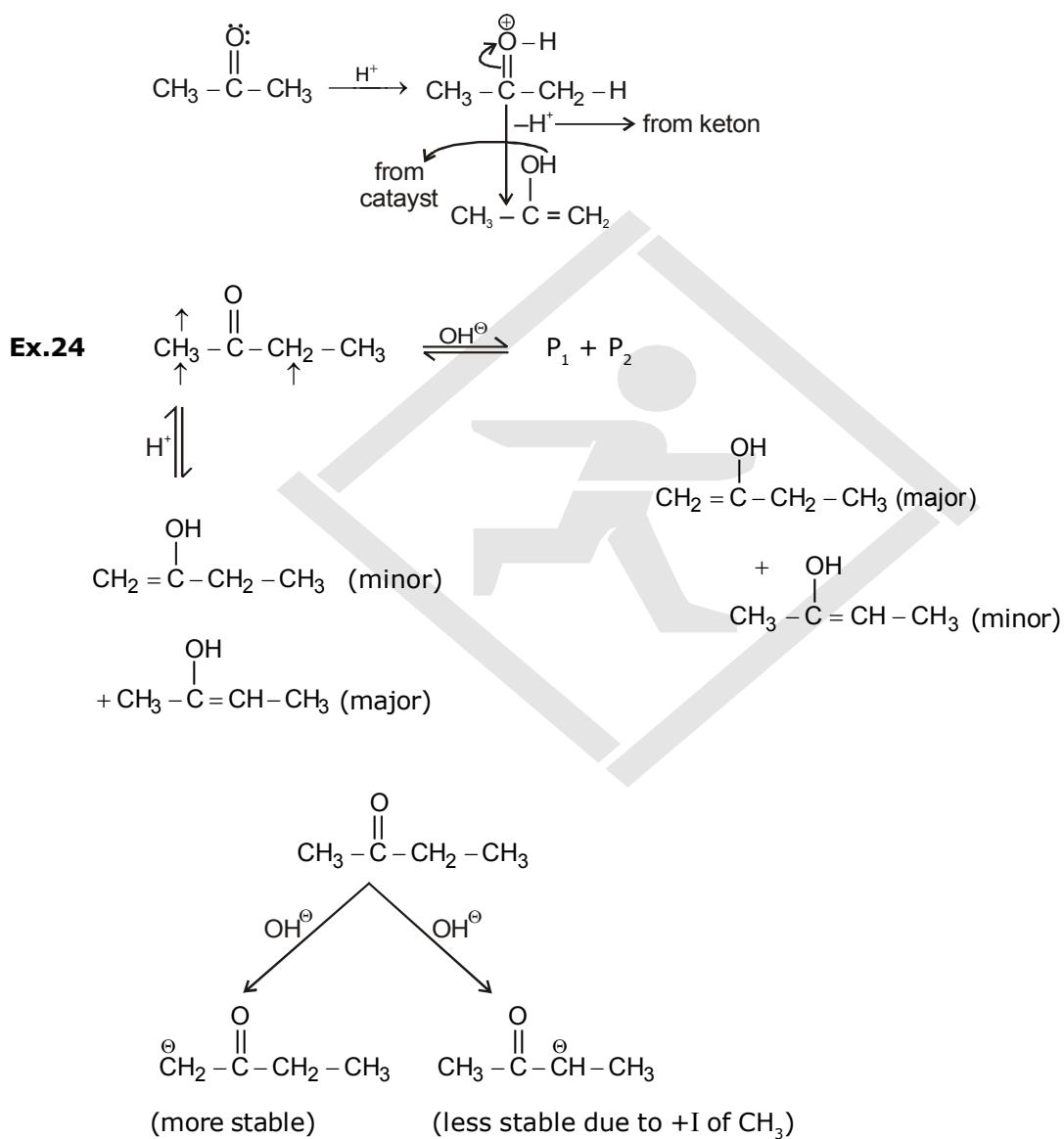


- * enol is more acidic than keto.
- * After removal of H^+ from both form.

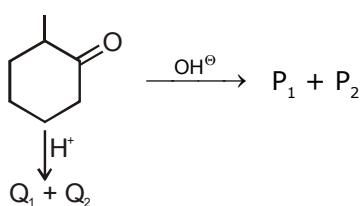
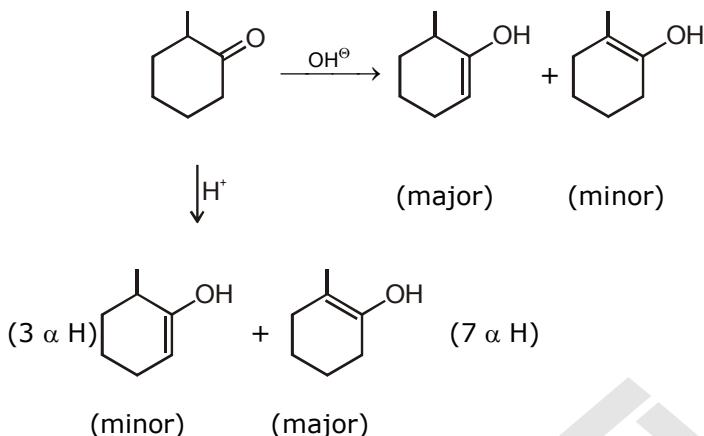
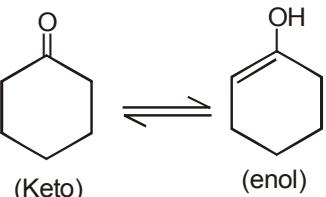


In Ist -ve charge is on C and in IInd -ve charge is on O therefore (ii) is more stable than (i) hence enol form is more acidic than keto form.

Acid Catalysed Tautomerism :

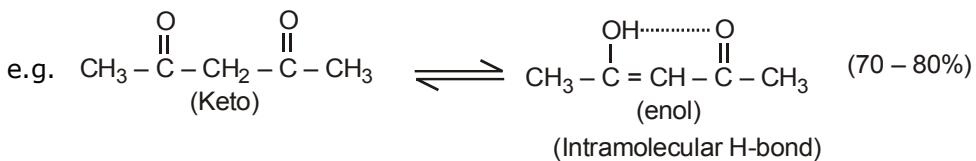


- * In case of base catalysed tautomerism the stability of carbanion is the deciding factor.
- * For acid catalysed tautomerism the stability at the product will be the deciding factor.

Ex.25**Sol.****Ex.26****Write the enol form****Sol.**

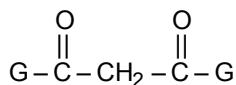
- * Generally keto form is more stable than enol but in some cases the stability of enol form is greater than keto. This is due to

(i) Intramolecular H-bonding	(ii) Aromatic character
(iii) Extended conjugation	(iv) Steric factor

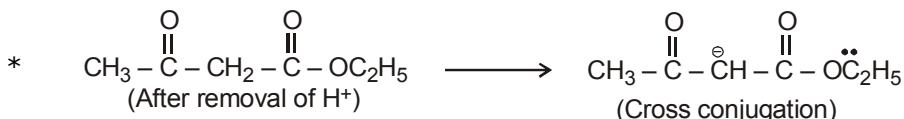


* Due to intramolecular H-bonding formation of 6 member ring takes place which is the cause of stability.

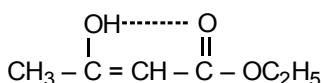
* This can be also summarised as



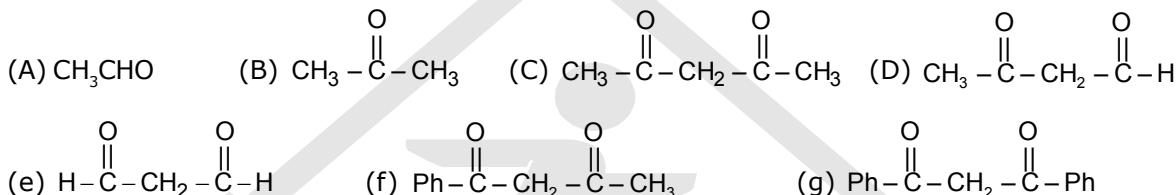
If G = H	% of enol	80 – 90%
G = Ph	% of enol	90 – 99%
G = CH ₃	% of enol	70 – 80%
G = OC ₂ H ₅ (one side)	% of enol	5 – 10%



* Cross conjugation restricts the Resonance.



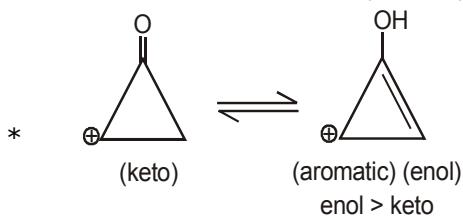
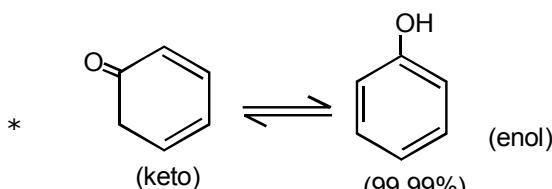
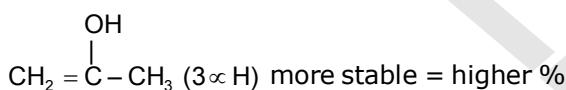
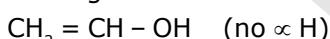
Ex.27 Compare the enol percent.

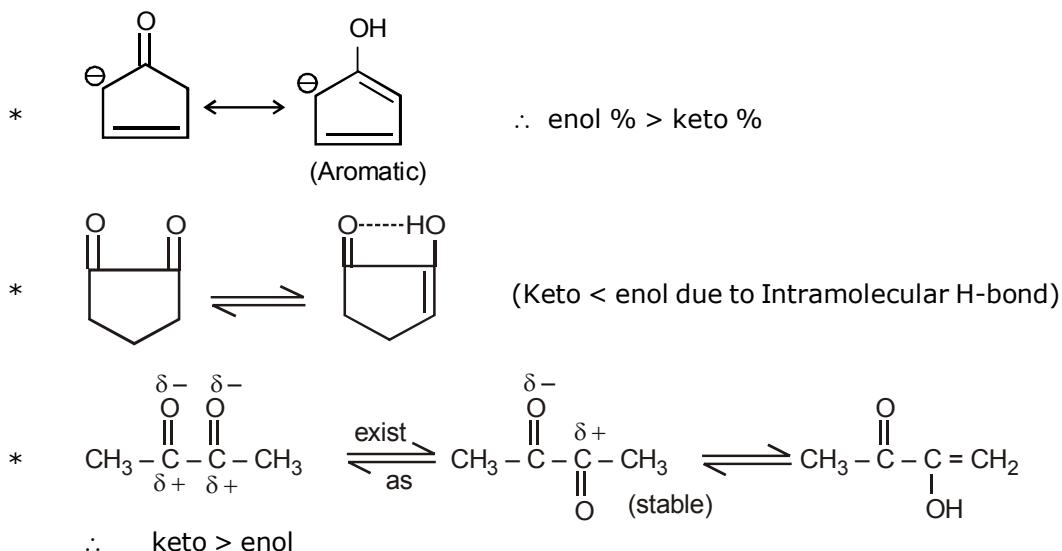
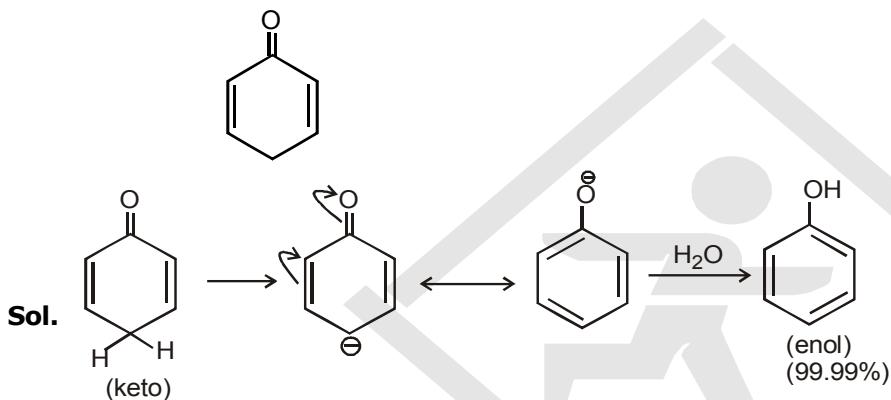


Sol. g > f > e > d > c > b > a

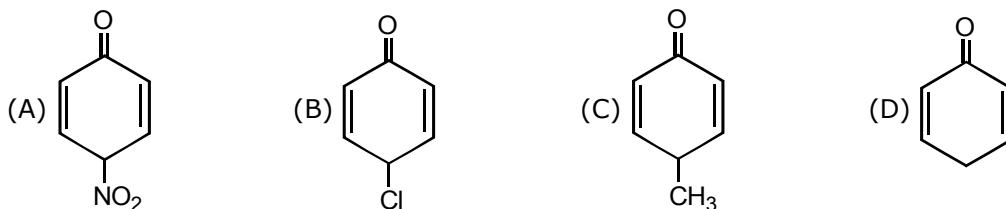
* Incase of a and b

After forming enol form

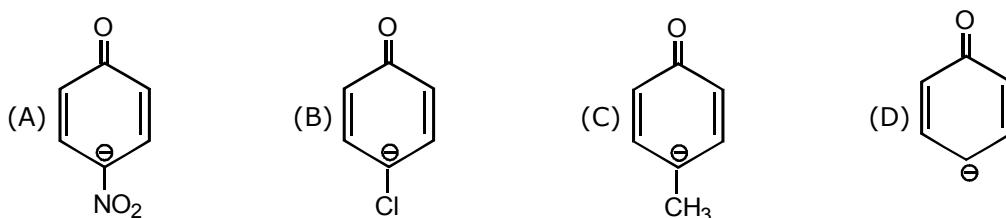


**Ex.28 Find the enol form the given compound.**

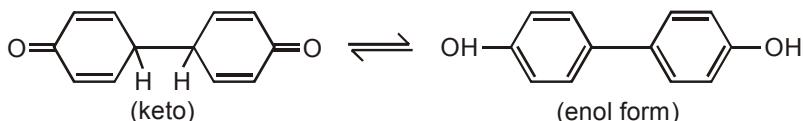
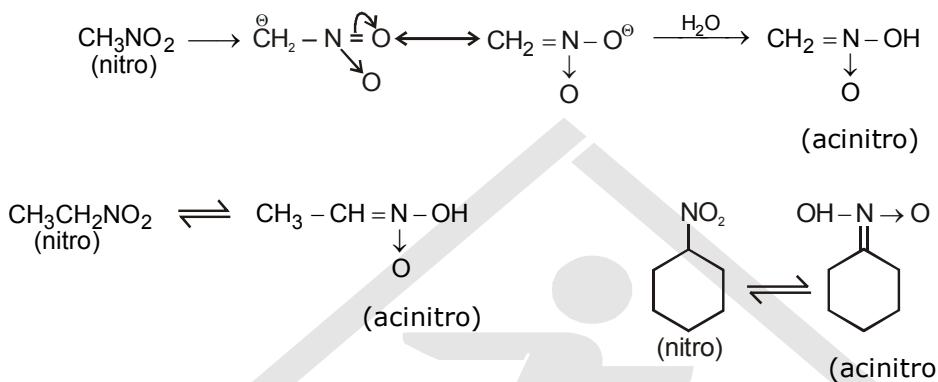
* Above case is called paratautomerism.
Here γ -Hydrogen participate in tautomerism.

Ex.29 Compare the enol content

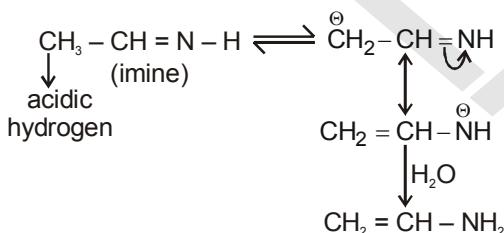
Sol. After removing H^+ (acidic-H) from the compounds



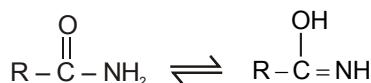
- * Enol percent \propto stability of carbanion
a > b > d > c
- * Formation of carbanion is one of step of from keto to enol. Therefore can be calculated as enol percent \propto stability of carbanion.

Ex.30 Find the enol form of**NITRO AND ACINITRO FORM**

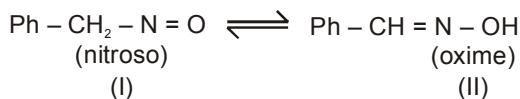
- * $(\text{CH}_3)_3\text{C}-\text{NO}_2$ will not show nitro and acinitro form it has no α H w.r.t to NO_2 group.

IMINE AND ENAMINE

- * For this type of tautomerism, there must α H w.r.t. ($-\text{CH}=\text{NH}$) group.

AMIDE AND IMIDOL

NITROSO AND OXIME FORM

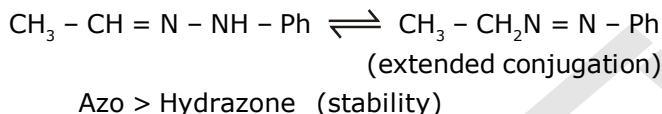
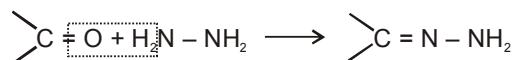


II > I (stability)

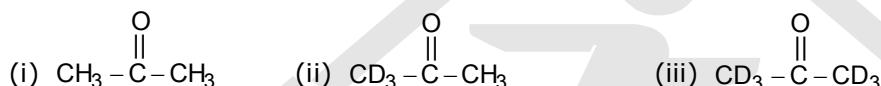
due to extended conjugation in (II)

HYDRAZONE AND AZOFORM

NH_2NH_2 (Hydrazine)



Ex.31 Compare enol percent.



Sol. As we know $\text{C} - \text{D} > \text{C} - \text{H}$ (Bond strength)

$\Rightarrow \text{C} - \text{D}$ will not break easily.

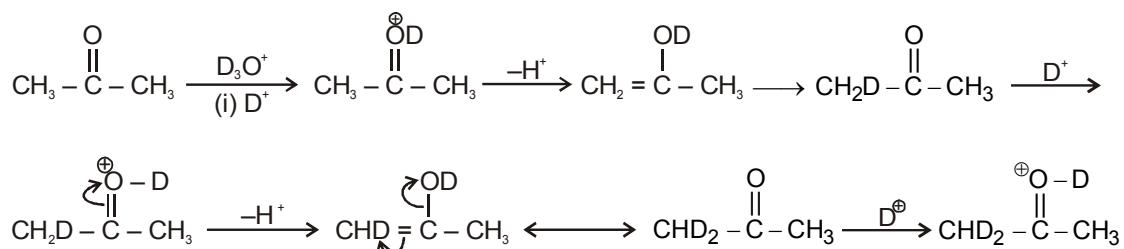
\Rightarrow Compound will have less tendency to come into enol form as $\text{C} - \text{D}$ bond breaking is one of the step for conversion of keto into enol.

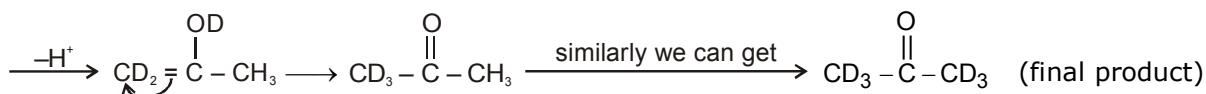
\Rightarrow enol percent will be less.

\Rightarrow (i) > (ii) > (iii) (enol content)

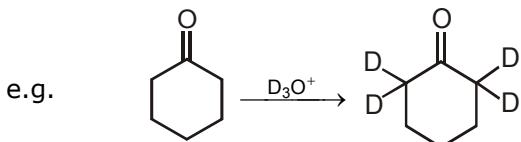
DEUTERIUM EXCHANGE REACTION

(Deuterium Exchange Tautomerism)





- To get the product directly replace all α -hydrogen w.r.t. carbonyl group by D(Deuterium)

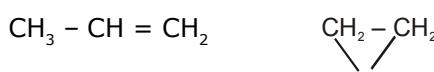


RING-CHAIN ISOMERISM

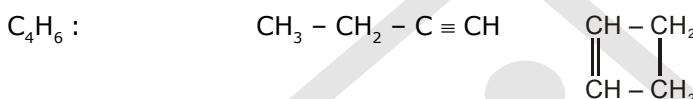
If one isomer has open chain structure and the other has cyclic structure then isomers are known as ring-chain isomers and isomerism between them is known as ring-chain isomerism.

For examples :

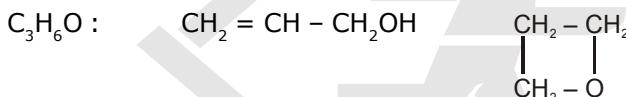
(i) Alkene and cycloalkane, ($C_n H_{2n}$)



(ii) Alkyne and cycloalkene, ($C_n H_{2n-2}$)



(iii) Alkenols and cyclic ethers, ($C_n H_{2n} O$)



Note : Ring-chain isomers are always functional isomers.

GEOMETRICAL ISOMERISM

Definition :

Isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to restricted rotation are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

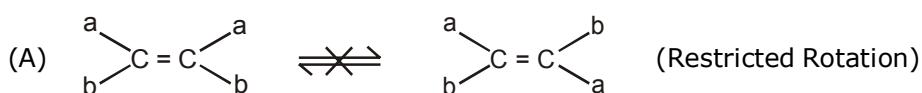
CONDITIONS OF GEOMETRICAL ISOMERISM

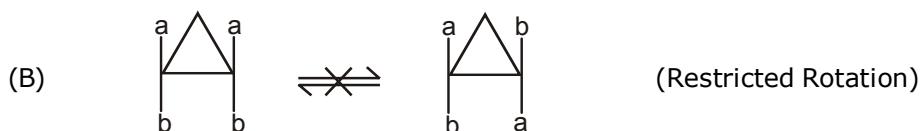
(I) Geometrical isomerism arises due to the presence of a double bond or a ring structure

(i.e. $\text{C}=\text{C}$, $\text{C}=\text{N}$ –, – $\text{N}=\text{N}$ – or ring structure)

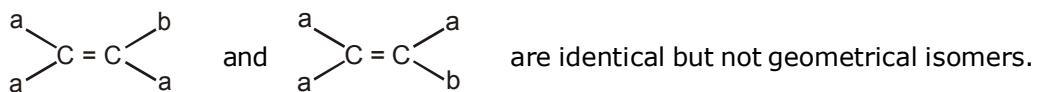
Due to the rigidity of double bond or the ring structure to rotate at the room temperature the molecules exist in two or more orientations. This rigidity to rotation is described as restricted rotation / hindered rotation / no rotation.

e.g.

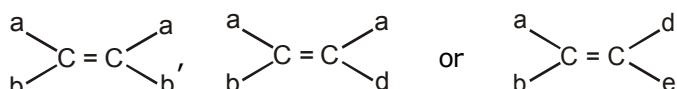




(II) Different groups should be attached at each doubly bonded atom. For example

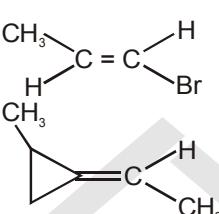
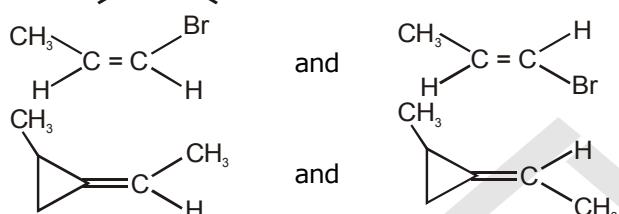


On the other hand, following types of compounds can exist as geometrical isomers :

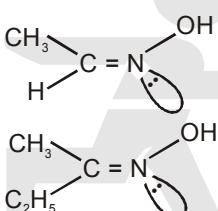
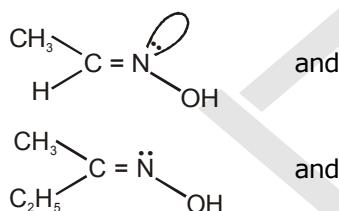


Examples of Geometrical isomers :

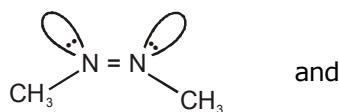
(I) Along $\text{C}=\text{C}$ bond



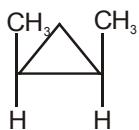
(II) Along $\text{C}=\text{N}$ bond



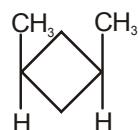
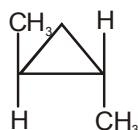
(III) Along $\text{N}=\text{N}$ bond



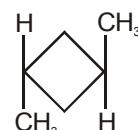
(IV) Along σ bond of cycloalkane



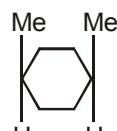
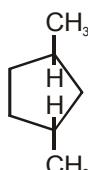
and



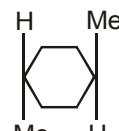
and



and

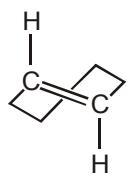


and



(V) Along $\begin{array}{c} > \\ \diagup \quad \diagdown \\ C = C \\ \diagdown \quad \diagup \end{array}$ in ring structures :

Usually in cycloalkenes double bond has its configuration. Their trans isomers do not exist due to large angle strain. But if the ring is large enough a trans stereoisomer is also possible. The smallest trans cycloalkene that is stable enough to be isolated & stored is trans-cyclooctene.



trans-cyclohexene
highly unstable
(non existant)



trans-cyclooctene
less stable than cis
(isolable at - 90°C)

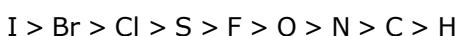
Configurational nomenclature in geometrical Isomerism

Configuration	Criteria	Remarks
cis / trans	Similarity of groups	If the two similar groups are on same side of restricted bond the configuration is cis otherwise trans.
E/Z	Seniority of groups	If the two senior groups are on same side of restricted bond the configuration is Z (Z = zusammen = together) otherwise E (E = entgegen = opposite).

Sequence rules : (Cahn - Ingold - Prelog sequence rules)

For deciding the seniority of groups following rules are applied :

Rule I : The group with the first atom having higher atomic number is senior. According to this rule the seniority of atom is :

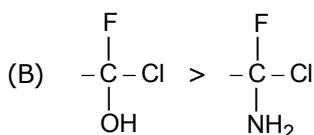


Rule II : The higher mass isotope is senior.

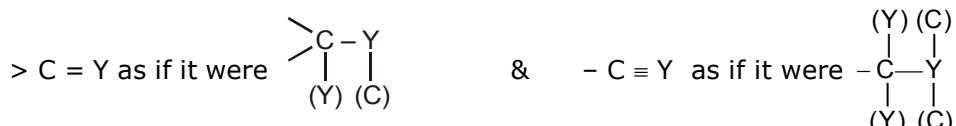
Thus (A) - T > - D > - H. (B) - C¹⁴H₃ > - C¹²H₃

Rule III : If the first atom of group is identical then second atom is observed for seniority.

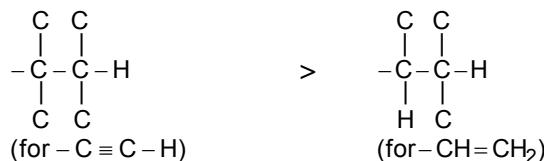
e.g. (A) - CH₂Cl > - CH₂OH > - CH₂NH₂ > - CH₂CH₃ > - CH₃



Rule IV : Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated that



e.g. for deciding seniority among $-\text{C} \equiv \text{CH}$, $-\text{CH} = \text{CH}_2$, their hypothetical equivalents are compared.



Rule V : Bond pair gets priority over lone pair.

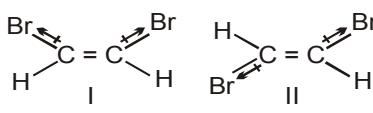
Rule VI : Z > E & R > S.

Number of Geometrical Isomers :

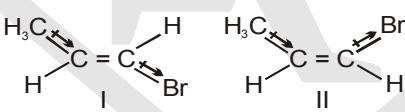
Number of geometrical isomers can be found by calculating the number of stereocentres in the compound. (stereocentre is defined as an atom or bond bearing groups of such nature that an interchange of any two group will produce a stereoisomer).

Nature of compound	No. of G.I. (n = no. of stereocentres)	Example	No. of Isomers	Isomers
(I) Compound with dissimilar ends	2^n	$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{C}_2\text{H}_5$	4	I : (cis, cis) II : (trans, trans) III : (cis, trans) IV : (trans, cis)
(II) Compound with similar ends with even stereocentres	$2^{n-1} + 2^{\frac{n}{2}-1}$	$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$	3	I : (cis, cis) II : (trans, trans) III : (cis, trans) \cong (trans, cis)
(III) Compound with similar ends with odd stereocentre	$2^{n-1} + 2^{\frac{n-1}{2}}$	$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$	6	I : (cis, cis, cis) II : (cis, cis, trans) \cong (trans, cis, cis) III : (cis, trans, trans) \cong (trans, trans, cis) IV : (trans, trans, trans) V : (cis, trans, cis) VI : (trans, cis, trans)

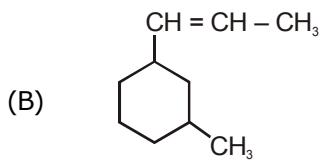
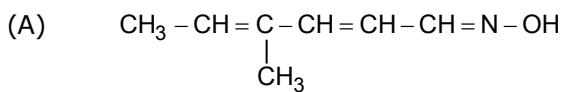
Physical Properties of Geometrical Isomers :

Physical properties		Remarks
Dipole moment	I > II	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out
Boiling point	I > II	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction
Solubility (in H ₂ O)	I > II	More polar molecules are more soluble in H ₂ O
Melting point	II > I	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.
Stability	II > I	The molecule having more vander waal strain are less stable. In cis isomer the bulky groups are closer they have larger vander waals strain.

Table

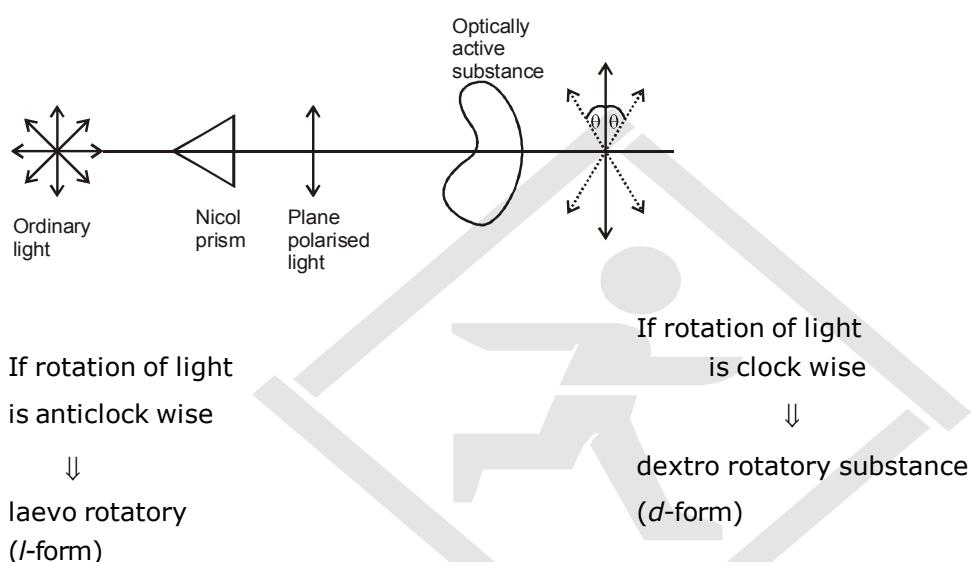
Physical properties	
Dipole moment	I > II
Boiling point	I > II
Solubility (in H ₂ O)	I > II
Melting point	I > II
Stability	I > II

Unsolved problem : Find the number of geometrical isomers in



Unsolved problem : Compare the physical properties (μ , b.p., m.p., solubility & stability) in the geometrical isomers of $\text{CH}_3 - \text{CH} = \text{CH} - \text{CN}$.

OPTICAL ISOMERISM

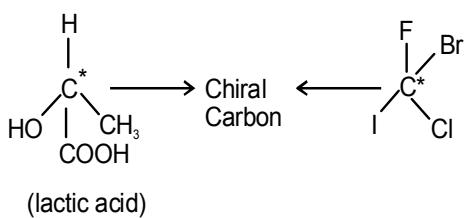


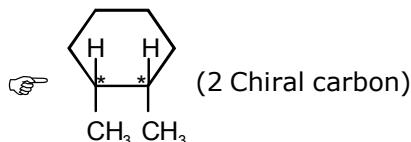
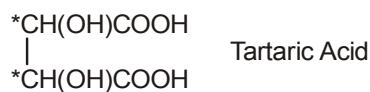
☞ If there is no rotation of light then substance is called optically inactive.

CHIRAL CARBON

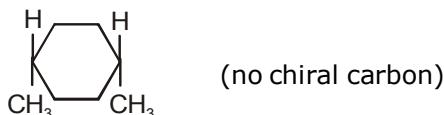
If all the four valencies of carbon are satisfied by four different atom or four different group atom then carbon is known as chiral carbon.

e.g.





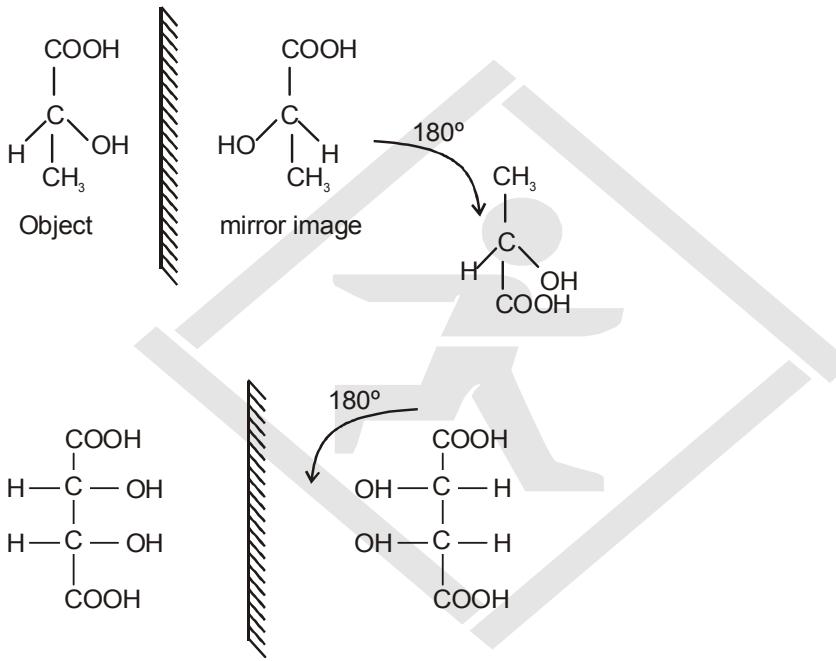
👉 Chiral carbon ढूँढ़ने के लिए पहले point of doubt check करना चाहिए



☞ For optically active isomer the object and its mirror image must be non superimposable.

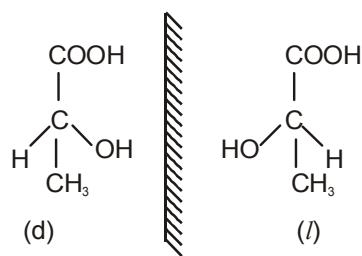
☞ If image and object are superimposable then they are not optically isomer to each other.

☞ To check, superimposable either of object or mirror image is rotated 180° along the mirror. After that mirror image is checked for superimposable.



⇒ After 180° rotation, mirror image and object are identical.(mirror image of meso compound will be identical)

If the compound have only one chiral carbon then it will be certainly optically active.



Object and its nonsuperimposable mirror image are called enantiomer to each other

32. A and B are enantiomer to each other. If specific rotation of A is $+20^\circ$ and rotation of mix of A and B is -10° then find the percentage of A and B in the mixture?

Sol. Let x mol A

(1-x) mol of B

$$\text{total rotational of A} = x \times 20$$

$$\text{total rotational of B} = (1 - x)(-20)$$

$$\text{Total rotation of the mixture} = -10$$

$$x \times 20 + (1 - x)(-20) = -10$$

$$20x - 20 + 20x = -10$$

$$40x = 10 \Rightarrow x = \frac{10}{40} = 0.25$$

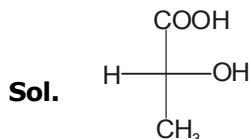
$$\Rightarrow \% \text{ A} = 25\%$$

$$\therefore \% \text{ B} = 75\%$$

FISHER PROJECTION

By fisher projection three dimensional structure is converted into 2D.

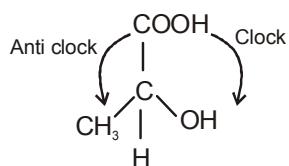
33. Write the Fisher projection of $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$



☞ Maximum carbon must be in vertical line.

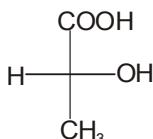
☞ Place higher priority carbon containing functional group on top of vertical line.

34. Write Fisher projection of

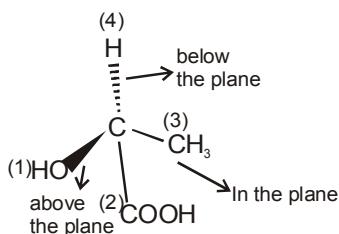


Sol. (i) Place higher priority carbon containing functional group on top of vertical line.

(ii) Arrange other group according to its clock wise or anticlock wise position w.r.t. group on the top.



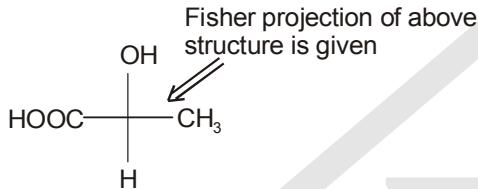
WEDGE DASH STRUCTURE



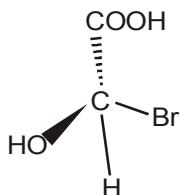
☞ केवल Fourth priority order को Cross कर सकते हैं, during checking of clock or anticlockwise.

☞ To draw Fisher projection of such structure

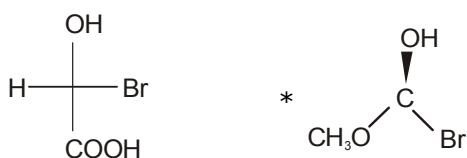
- (1) Dotted group is placed below
- (2) The group attached by dark line is placed on the top.
- (3) Remaining group are placed according to their clock wise or anticlock wise position w.r.t. group in dark line.



35. Draw the fisher projection of



Sol.



If fourth valency is not given then we assume it to be hydrogen

R AND S FORM

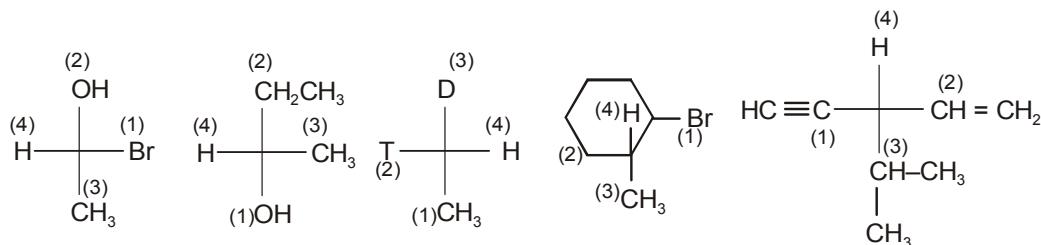
↷ R → Rectus → Right → Clock wise.

S → Sinister → Left → Anticlock wise.

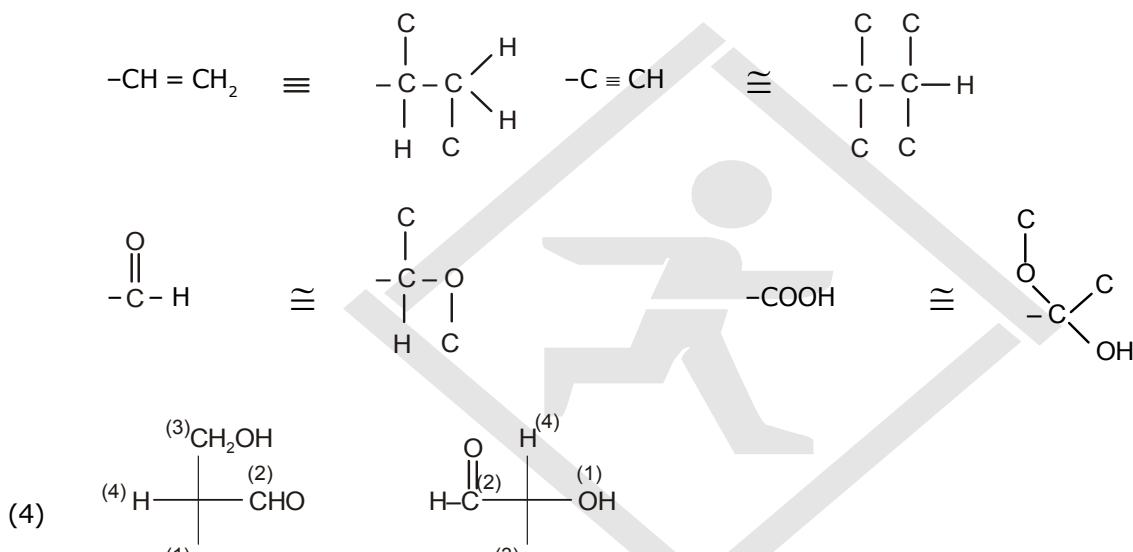
PRIORITY ORDER

Higher the atomic number of the element, greater will be its priority.

e.g.

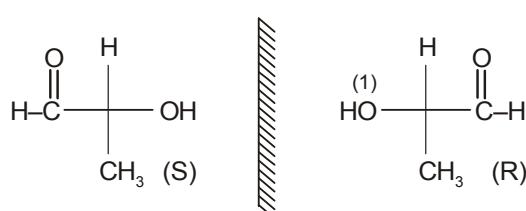


In case of double bond (=) or triple (≡) bond



1 → 2 → 3 If clock wise ⇒ R

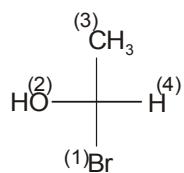
1 → 2 → 3 If Anti clock wise ⇒ S



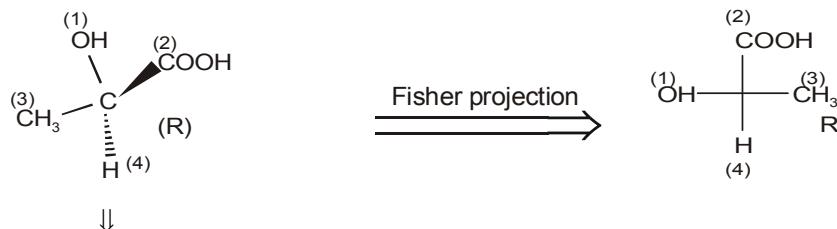
⇒ Mirror image of R is S

If lowest priority element is in horizontal then exact order is obtained by reversing the form (i.e. it comes R then exact form will be S and vice versa)

e.g.



⇒ It comes as R but will be S form,



If lowest priority order element is in dotted then

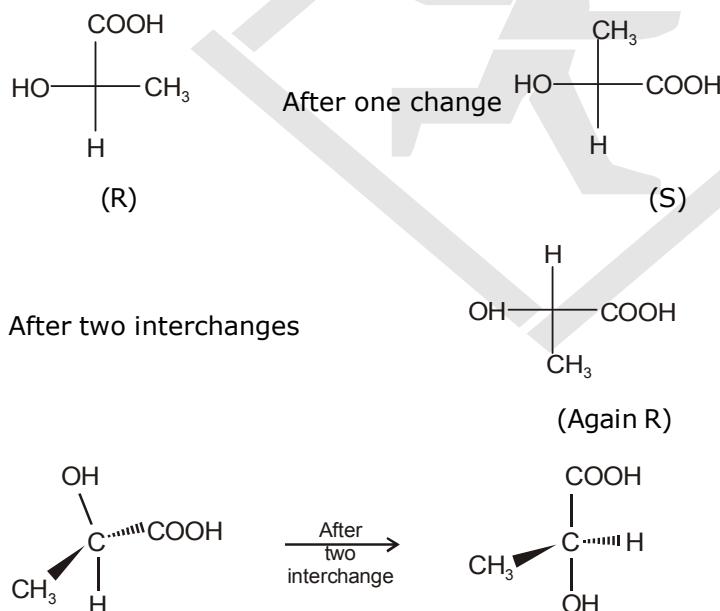
$1 \rightarrow 2 \rightarrow 3$ If clock wise ⇒ R

and if $1 \rightarrow 2 \rightarrow 3$ If Anti clock wise ⇒ S

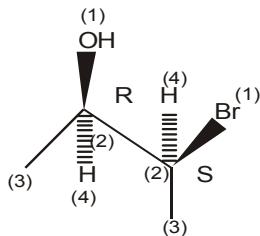
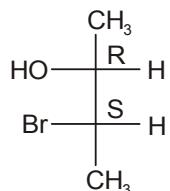
☞ If lowest priority order element is not in dotted then we bring it in dotted by doing even number of inter changes (2, 4 or 6) as by even no. of inter change, the configuration does not change.

☞ After odd number of change the configuration changes (If R then goes into S and vice versa).

For Example:



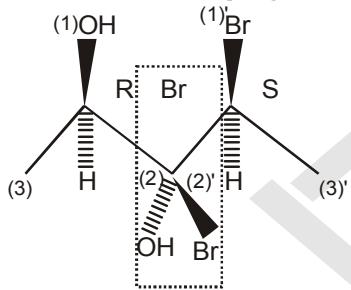
Ex.36 Draw the Fisher projection of

**Sol.**

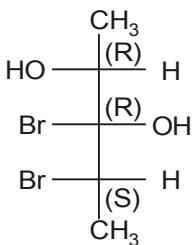
☞ All the carbons are placed in vertical

☞ Group attached to the chiral carbons are placed on any side. After that they are adjusted whether they are R or S form w.r.t chiral carbons.

Ex.37 Draw the Fisher projection of the following.



Wedge Dash formula

Sol.

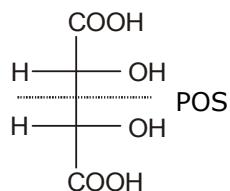
Fisher projection

RACEMIC MIXTURE

It is an equimolar mixture of R and S or *d* and *l*. Racemic mixture is optically inactive

☞ A compound is optically active due to

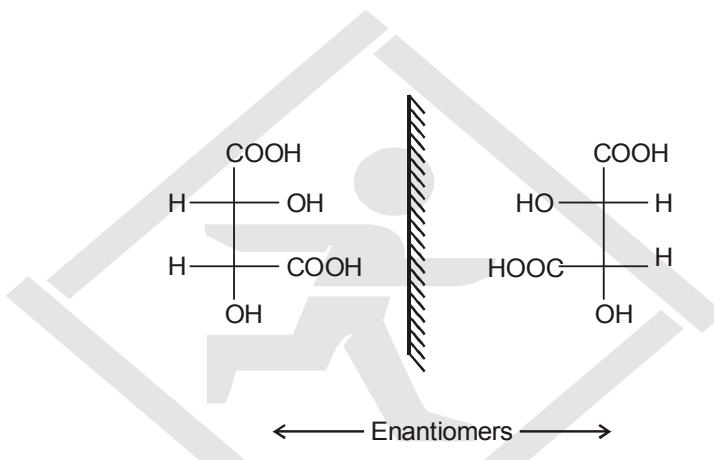
- (1) Absence of plane of symmetry (POS)
- (2) Absence of centre of symmetry (COS)



(meso form)

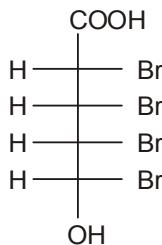
- ☞ POS is an imaginary plane where if we place a mirror, mirror image will exactly overlap the other half.
- ☞ For meso form, there must be at least two identical chiral carbon.
- Identical carbon \Rightarrow Chiral carbons having identical group attached.
- ☞ If compound has POS then it will be certainly optically inactive and will be called meso form.
- ☞ After finding two identical carbons. We assign them as R or S. If first part is R and other is S then they will rotate the light in opposite direction but to equal extent the compound will be optically inactive

(meso form)



- ☞ If a compound have 'n' different chiral carbon then total no. of optically active isomers = 2^n
- No. of meso form = 0

e.g.



no. of different chiral carbon = 4
total optical isomer = $2^n = 2^4 = 16$

- ☞ There will be no meso as the compound does not have identical chiral carbon.

☞ If a compound has n identical chiral centre (symmetrical) \Rightarrow There must be symmetry from somewhere.

(i) If n is even

$$\text{optical isomer (a)} = 2^{n-1}$$

$$\text{mesoform (m)} = 2^{\frac{n}{2}-1}$$

$$\text{total optical isomer} = a + m$$

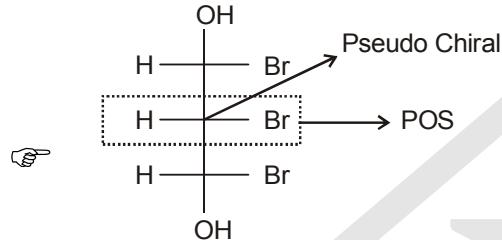
(ii) If n is odd

$$a = 2^{n-1} - 2^{\frac{n-1}{2}}$$

$$m = 2^{\frac{n-1}{2}}$$

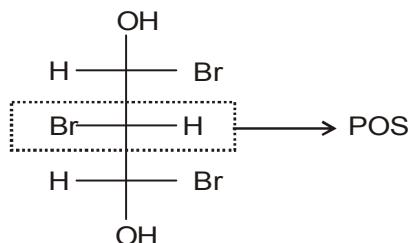
$$\text{Total optical isomer} = 2^{n-1} - 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}}$$

$$= 2^{n-1}$$



☞ When there is odd no. of identical carbon atom (i.e. symmetrical) then this compound will certainly contain pseudo chiral w.r.t. to which compound be symmetrical (i.e. POS)

☞ Other meso compound of the above compound will form by changing the place Br and H around Pseudo Chiral carbon.



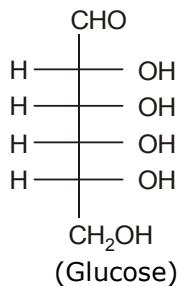
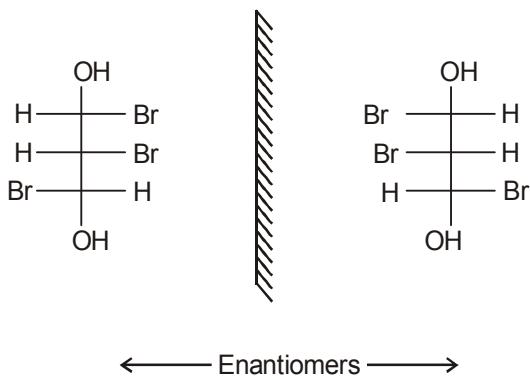
$$\text{Total meso} = 2$$

$$\text{optical} = 2^{n-1} - 2^{\frac{n-1}{2}}$$

$$= 2^{3-1} - 2^{\frac{3-1}{2}}$$

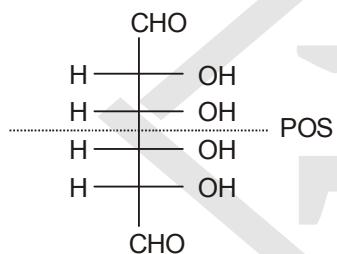
$$= 2^2 - 2$$

$$= 4 - 2 = 2$$



Total no. of different chiral carbon = 4

Total optical isomer = $2^4 = 16$



Total no. of even chiral = 4

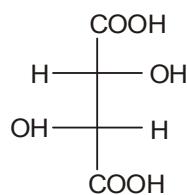
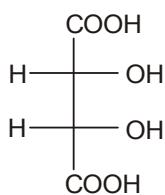
$$a = 2^{n-1} = 2^{4-1} = 2^3 = 8$$

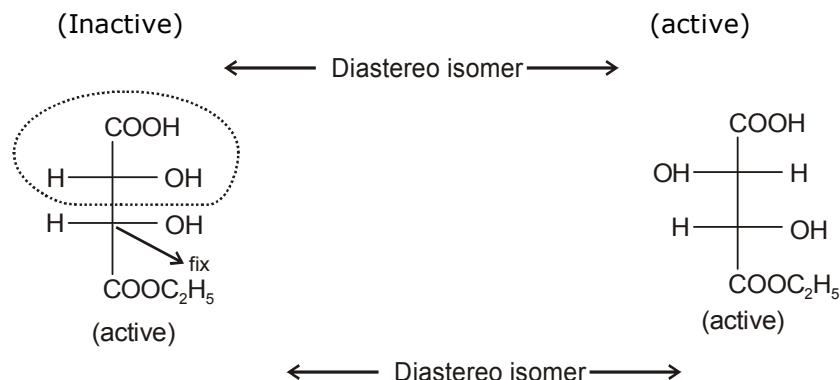
$$m = \frac{n-1}{2} = \frac{4-1}{2} = 2^{2-1} = 2^1 = 2$$

$$\text{Total isomer} = 8 + 2 = 10$$

DIASTERO ISOMERS

☞ For single chiral centre, there is no diastereoisomer. The stereoisomer which are not related as object and mirror image. They may be optically active or optically inactive.



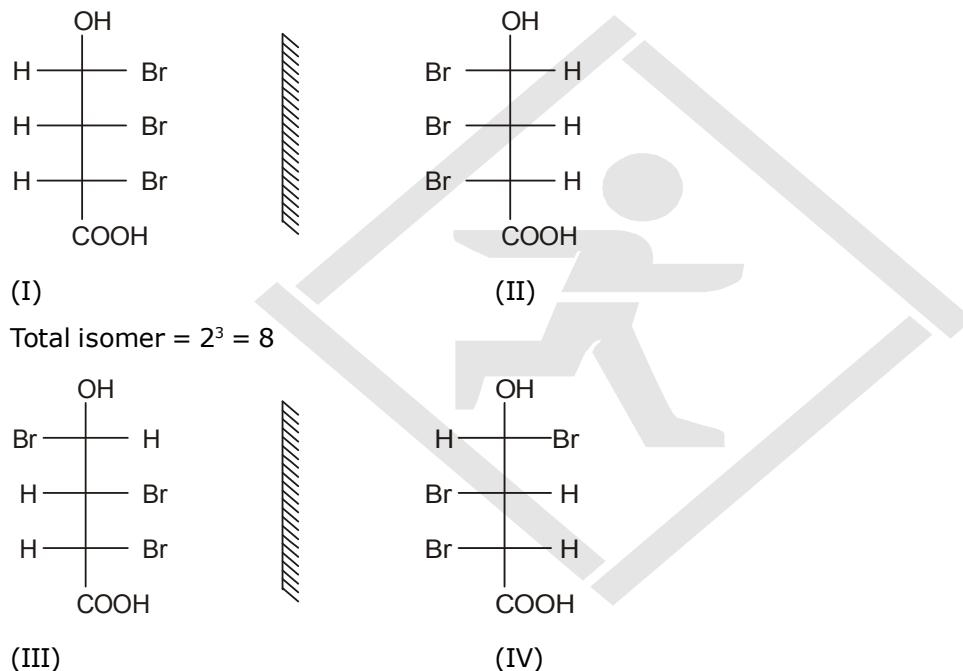


 Fix one chiral carbon

After one inter change

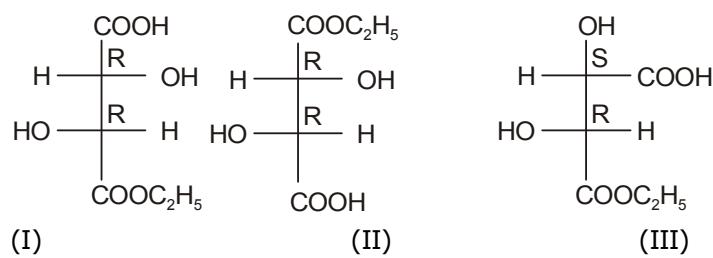
If $(R, R) \rightarrow (R, S)$

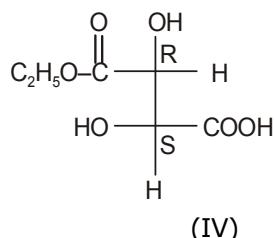
For compound having 3 chiral carbon to get diastereoisomer, fix two chiral carbon and one interchange with left carbon or fix one chiral carbon and inter change with other two,



(I) and (III), I and (IV), (II) and (III), (II) and (IV) are diastereoisomers.

Ex.38



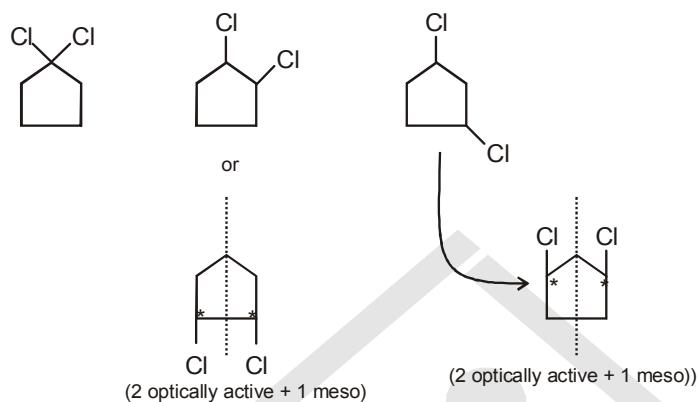


What are the relation among the above compounds?

Sol. I and II are identical III and IV are identical
 II and III are diastereoisomer I and IV are diastereoisomer

Ex.39 Find total isomers obtained by dichlorination of cyclopentane?

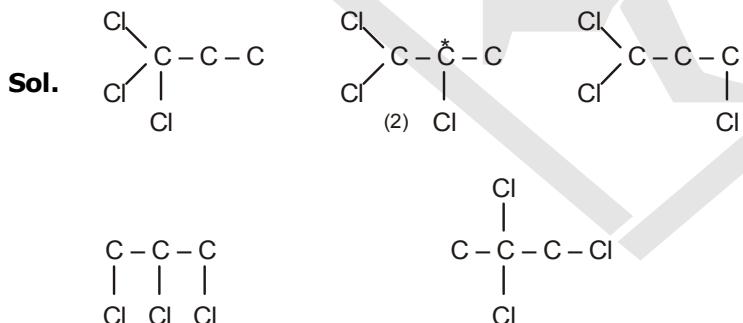
Sol.



$$\text{Total isomers} = 3 + 3 + 1 = 7$$

$$\text{Optically isomers} = 6, \text{ Optically active isomers} = 4$$

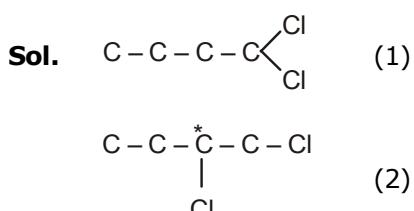
Ex.40 Find the total isomers obtained by trichlorination of propane.

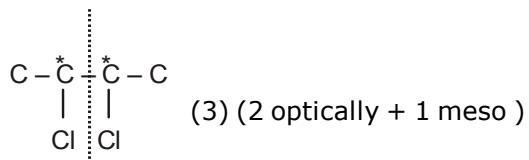
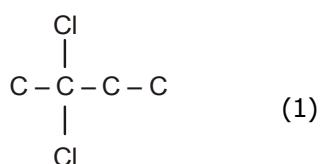
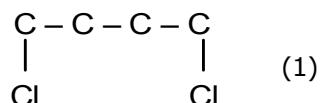
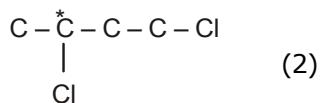


$$\text{Total isomers} = 6$$

$$\text{optically isomers} = 2$$

Ex.41 Find total isomers obtained by dichlorination of n-butane

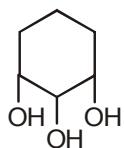




Total isomers = 10 (6 optically active + 1 meso + 3 structural)

Ex.42 How many stereoisomers of 1,2,3-cyclohexanetriol

Sol.

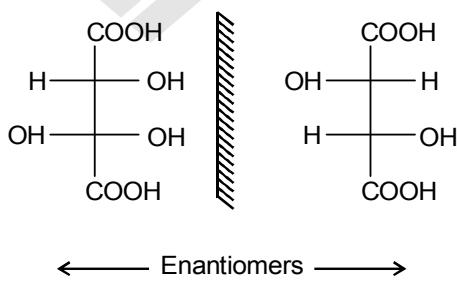
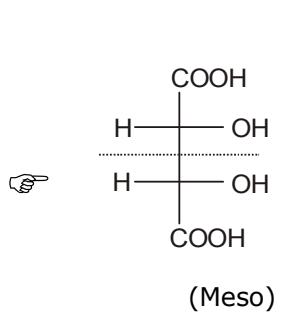


No. of Chiral carbon = 3 (identical) symmetrical

$$a = 2^{n-1} - 2^{\frac{n-1}{2}} = 2^{3-1} - 2^{\frac{3-1}{2}} = 4 - 2$$

$$m = 2^{\frac{n-1}{2}} = 2^{\frac{3-1}{2}} = 2$$

$$\text{total stereoisomers} = 2 + 2 = 4$$



☞ Mesoform is optically inactive due to internal compensation and racemic mixture is optically inactive due to external compensation.

Ex.43 A and B are enantiomer of each other. Specific rotation of A is 20° . Rotation of mixture of A and B = -5° what is the percentage of racemic part?

Sol. $x \text{ mol A, } 1-x \text{ mol B}$

$$x \times 20 + (1-x)(-20) = -5$$

$$20x - 20 + 20x = -5$$

$$40x = 15 \Rightarrow x = \frac{3}{8} = 0.375$$

$$\text{moles of A} = \frac{3}{8}$$

$$\text{moles of B} = 1 - \frac{3}{8} = \frac{5}{8}$$

$\frac{3}{8}$ moles of A and $\frac{5}{8}$ moles of B will form racemic mixture.

$$\text{Enantiomer excess or optical purity} = \frac{5}{8} - \frac{3}{8} = \frac{2}{8} = \frac{1}{4}$$

Ex.44

- specific rotation of A is $+20^\circ$
- mixture is 70% racemic.
- 30% of pure B.

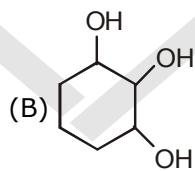
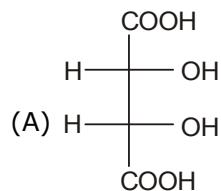
What is rotation of mixture?

Sol. Rotation will be due to B only,

$$\begin{aligned} &= 0.3 \times (-20^\circ) \\ &= -6^\circ \end{aligned}$$

☞ Chiral compound → optically active compound

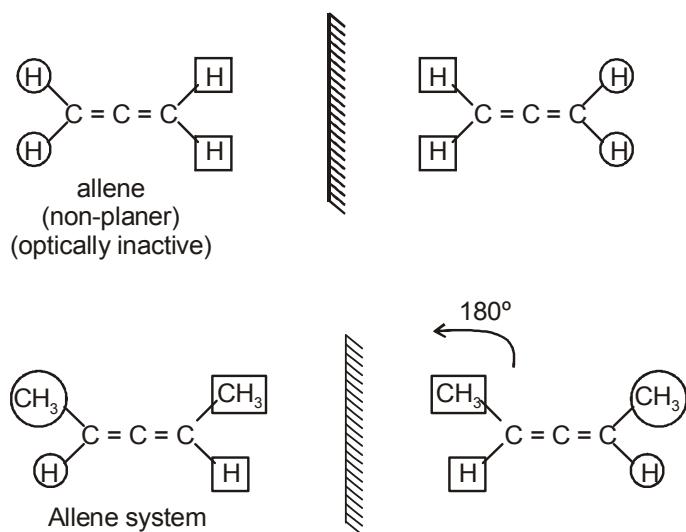
Ex.45 Which of the following compound is Chiral (Optically active)?



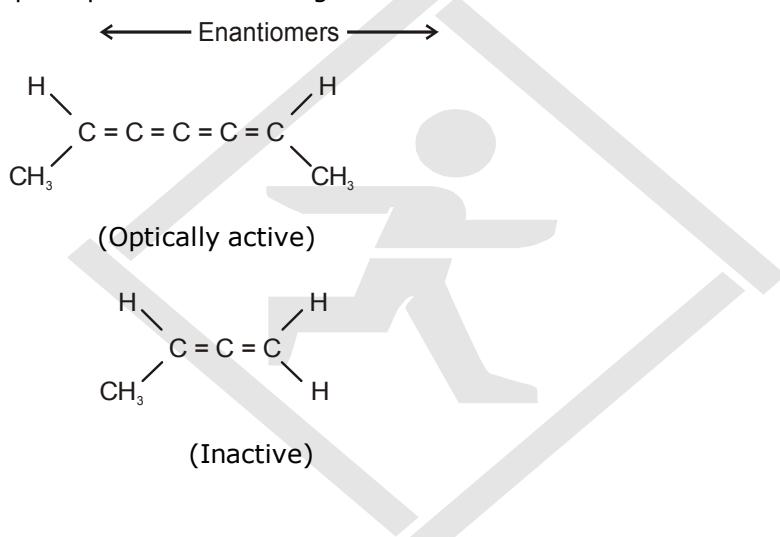
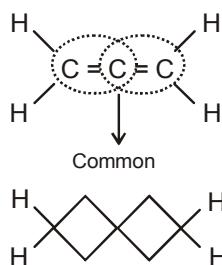
(C) Both

(D) None

Ans. (D)

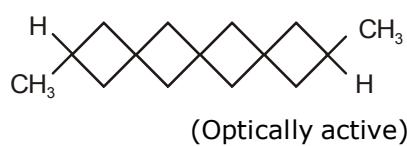
ALLENE SYSTEM

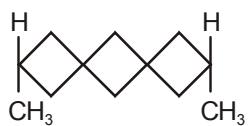
They are non superimposable.mirror image

SPIRO COMPOUNDS

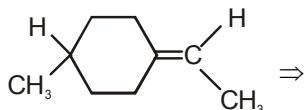
If no. of rings are even \Rightarrow optically active

If no. of rings are odd \Rightarrow Inactive





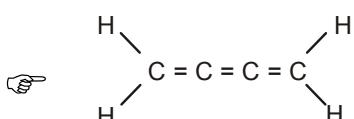
(Optically Inactive)



⇒ This is the even no of double bond case.

(Optically active)

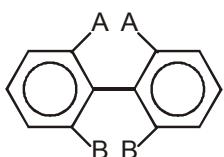
☞ For optical activity, the carbons at extreme position must have different group attached.



⇒ Planer compound

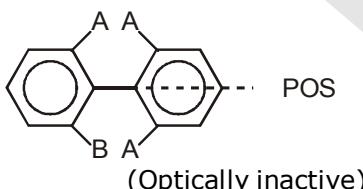
Always have POS ∴ Optically inactive

BIPHENYLS

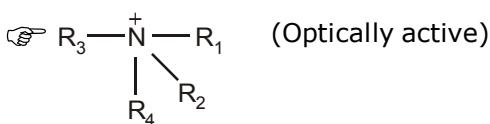


If biphenyl contain bulky group at its ortho position (only) then due to repulsion the planarity of compound disappears and its mirror image is non superimposable.

☞ In the biphenyls none of the two ring must have symmetry.

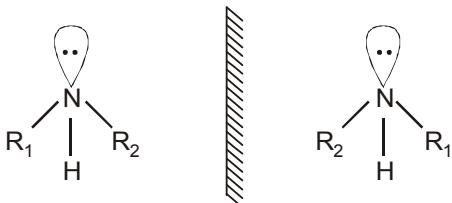


(Optically inactive)



(Optically active)

In 2° Amines.



Optically inactive due to formation of racemic mixture.

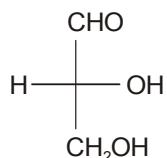
☞ Order of flipping in amines $1^\circ > 2^\circ > 3^\circ$

D-Form :- For compound having one chiral carbon

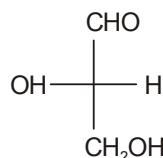
(a) If OH is right side \rightarrow D

(b) If OH is left side \rightarrow L

(Note \rightarrow All the carbon must be in vertical having highest O. N. Carbon on the top)

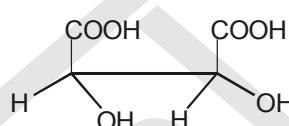
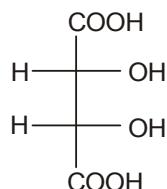


D-form



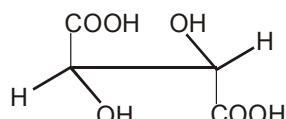
L-form

CONVERSION OF FISHER PROJECTION IN SAWHORSE STRUCTURE

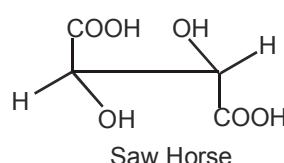
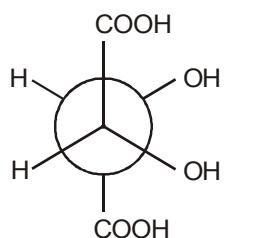


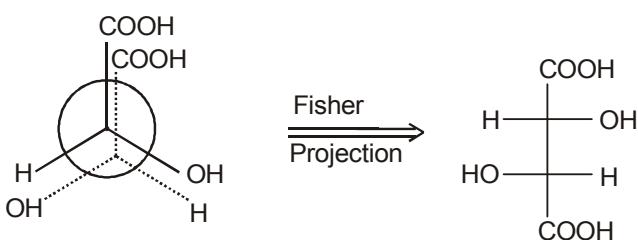
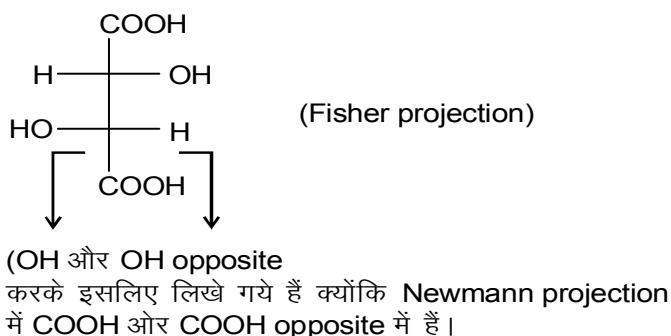
☞ सबसे पहले, First Chiral Carbon को As it is लिख लेते हैं। फिर अगर दोनों Vertical वाले group, same side में हैं, तो दूसरे chiral carbon के, Respect में बाकी दोनों group जैसे लगे हैं वैसे ही लगा देगे जैसे उपर वाले example में दूसरे chiral में, Left में H और Right में OH हैं तो उसे वैसे ही Place कर देगे।

☞ और दोनों Vertical में situated group को opposite में place करेगे तो दूसरे वाले Chiral से attached बाकी दोनों group का side reverse कर देगे i.e. left वाले group को Right में और Right वाले group को left में place कर देगें।
The above Fisher projection can also written in Saw Horse form as follows



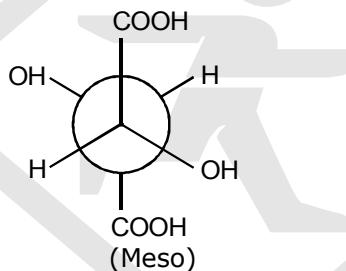
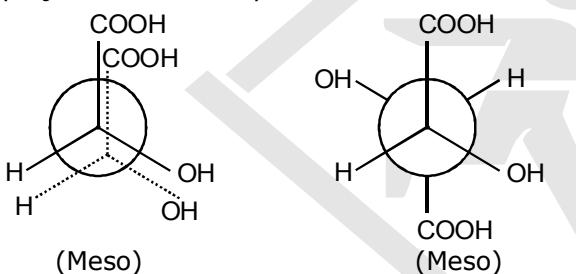
CONVERSION OF NEWMANN PROJECTION IN TO SAWHORSE PROJECTION





Above example में दोनों COOH, same side में हैं। इसलिए second chiral carbon में के respect में लगे group का place बदला नहीं जायेगा।

If all the identical groups are same side or in exactly opposite direction to each other in Newmann projection then compound will be meso.

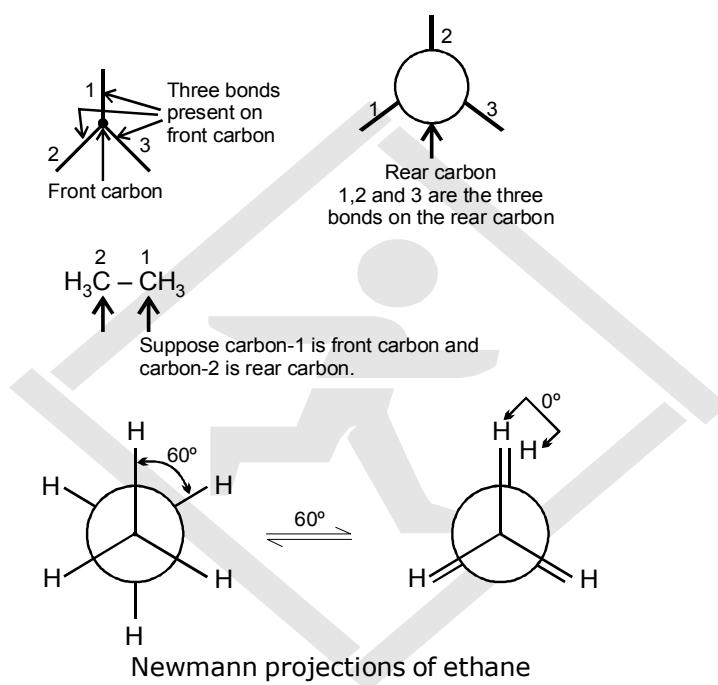


CONFORMATIONAL ISOMERS

Conformational Isomerism in Alkanes

Different spatial arrangements of the atoms that result from **restricted** rotation about a single bond are called conformations. Different conformations are also called conformational isomers or **conformers**.

When an ethane molecule rotates about its carbon-carbon single bond, two extreme conformations can result : the **staggered conformation** and the **eclipsed conformation**. An infinite number of conformations between these two extreme conformation is also possible . There are several ways to represent on paper the three dimensional conformation that, occur as a result of rotation about a single bond. **Wedge-and -dash structures**, **Sawhorse projections** and **Newmann** projections are all commonly used methods. But here we will use only Newmann projections. In a Newmann projection you will look down the length of a particular carbon-carbon single bond. The carbon that is in the front, is represented by the point at which three bonds intersect and the carbon that is in the back is represented by a circle. The three lines emanating from each of the carbons represent the carbon's other three bonds.



Staggered conformations : A conformation with a 60° dihedral angle is known as staggered conformation.

Eclipsed conformation : A conformation with a 0° dihedral angle is known as eclipsed conformation.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. The staggered conformation, therefore, is the most stable conformation because the carbon-hydrogen bond are as far away from each other as possible. The eclipsed conformation is the least stable conformation, because in no other conformation are the carbon-hydrogen bond closer to one another. In staggered conformation the distance between the hydrogen nuclei is 2.55 Å. but, they are only 2.29 Å apart in the eclipsed conformation. The rotational barrier in ethane is 2.9 Kcal/mole. This rotational barrier can be described in terms of the change in potential energy of the molecule as a function of the change in dihedral angle. The extra energy of the eclipsed conformation is called **torsional strain**. Torsional strain is the name given to the repulsion felt by bonding electrons of one substituent as they pass close the bonding electrons of another substituent. The energy barrier between staggered and eclipsed conformation in ethane molecule is 2.9 Kcal/mole (12 kJ/mole). This barrier is more than RT (\approx 0.6 Kcal/mole) at room temperature (energy for free rotation) and less than 16-20 Kcal/mole (energy barrier for frozen rotation). Hence the rotation

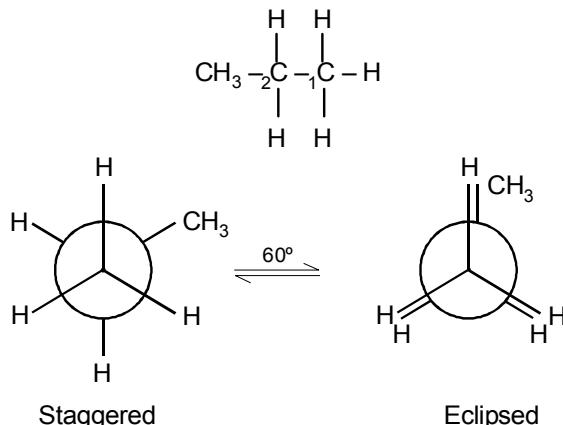
about carbon-carbon single bond is neither completely free nor frozen but only restricted.

Note : (i) For free rotation energy barrier is 0.6 Kcal/mole.

(ii) For restricted rotation energy barrier is in between > 0.06 and < 16 Kcal/mole.

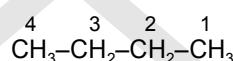
(iii) For frozen rotation energy barrier is \geq 16 Kcal/mole.

Similarly propane has also two conformations.

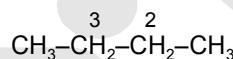


In this case, out of six substituents on two C's (carbon -1 and carbon-2) five, are hydrogens and one is CH₃ group.

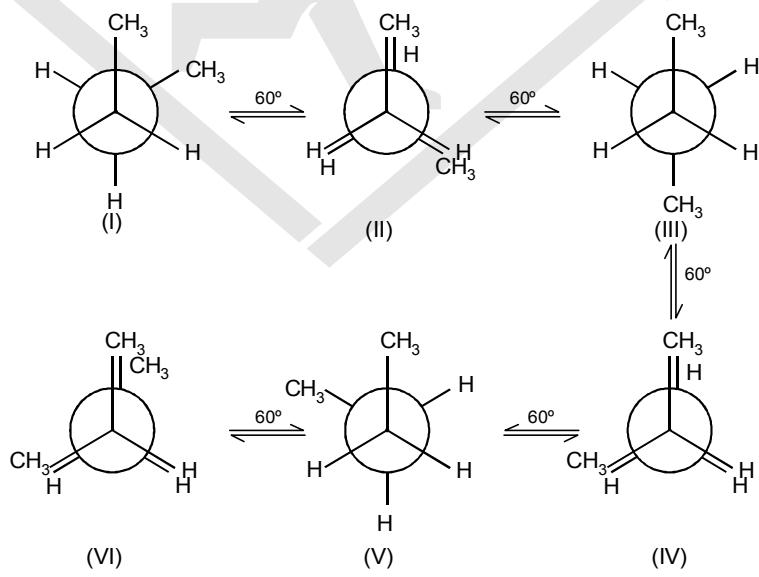
Butane has three carbon-carbon single bonds and the molecule can rotate about each of them



If rotation will be about C - 2 and C - 3 bond then conformation will be symmetrical.



For conformational analysis treat butane as the derivative of ethane. Out of six substituents four are hydrogens and two are methyl groups. Different conformations of butane are obtained by rotation.



Butane has three staggered conformers (I, III and V) .

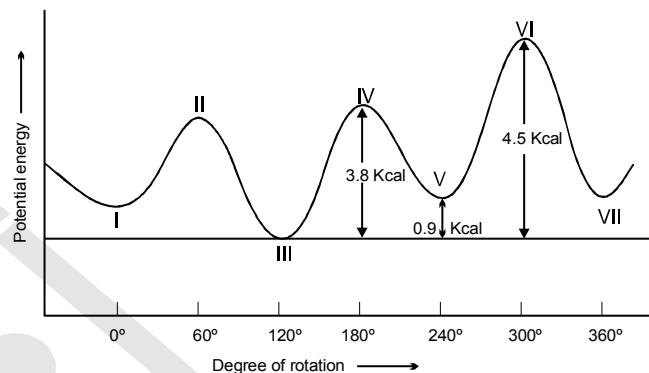
Conformer -(III), in which the two methyl groups are as far apart as possible, is more stable than the other two staggered conformers (I and V). The most stable of the staggered conformers is called the **anti conformer** (in anti conformation the angle between two methyl groups is 180°) and the other two staggered conformers are called gauche conformers. (anti in Greek for "opposite of" gauche in French for " left"). In gauche conformation the angle between two methyl groups is 60° .

In the anti conformer, the largest substituents (CH_3 and CH_3) are opposite to each other; in the gauche conformer, they are adjacent. Two gauche conformers have the same energy but each is 0.9 Kcal/mole less stable than the anti conformer.

Anti and gauche conformers do not have the same energy because of the steric strain. **Steric strain** or **steric hindrance** is the strain put on a molecule when atoms or groups are large in size and due to this they are too close to each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the anti because the two methyl groups are closer together in the gauche conformer. Steric strain in gauche conformer is called gauche interaction.

The eclipsed conformer in which the two methyl groups are closest to each other (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional strain is due to bond-bond repulsion and steric strain is due to the closeness of the eclipsing groups.

In general steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer (VI) is called the fully eclipsed conformer (angle between two methyl groups is zero) whereas (II) and (IV) are called eclipsed conformers. The energy diagram for rotation about the C-2-C-3 bond of butane is shown in the **Fig.**



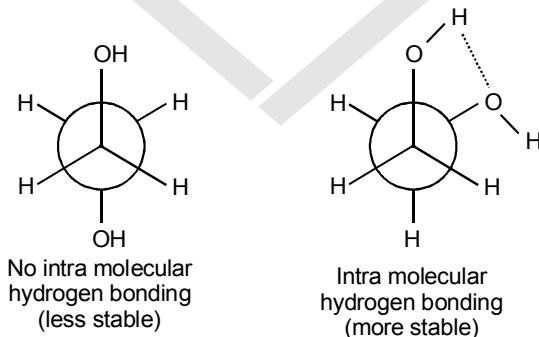
Thus the relative stabilities of the six conformers of n-butane in decreasing order is as follows:

Anti > gauche > eclipsed > fully eclipsed

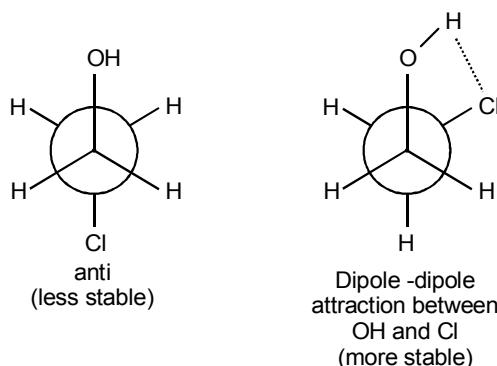
(III) (I) and (II) and (VI)

Thus molecules with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

Although anti conformation is more stable than the gauche conformation but in some cases gauche conformation is more stable than the anti because of the intramolecular hydrogen bonding which is geometrically possible only in the gauche conformation.

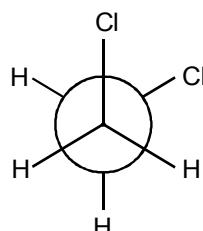


In ethylenechlorohydrin also gauche conformation is more stable than the anti conformation due to the dipole-dipole attraction between OH and Cl which is geometrically possible only in the gauche conformation.



Ex.46 Write Gauch conformation of the compound $\text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$?

Sol. Gauch conformation of the given compound is:



(i) Mole fraction of anti and gauch form : Mole fraction of stable conformers (i. e., mole fraction of anti and gauch can be calculated if dipole moment of anti and gauch form is known.

$$\mu_{ob} = \mu(\text{anti}) \times x_a + \mu(\text{gauch}) \times x_g$$

where x_a = mole fraction of anti form and
 x_g = mole fraction of gauch form.

Suppose

$$\begin{aligned}\mu_{ob} &= 1.00 \\ \mu_g &= 5.55\end{aligned}$$

Then x_a can be calculated as follows :

$$\begin{aligned}\mu_{ob} &= \mu_a \times x_a + \mu_g \times x_g \\ 1 &= 0 \times x_a + 5.55 x_g \\ x_g &= \frac{1}{5.55} = 0.18\end{aligned}$$

Sum of mole fraction of $x_a + x_g = 1$

$$x_a = 1 - x_g = 1 - 0.18 = 0.82$$

(ii) relative amounts of anti and gauch conformers

The anti conformer of n-butane is more stable than the gauch by about 900 Kcal/mole (i.e., 0.9 Kcal/mole). This is energy barrier between anti and gauch.

Thus



Suppose at room temp ΔG is negligible.

So

$$\Delta G = -RT \ln K_{eq}$$

$$K_{eq} = \frac{[\text{anti}]}{[\text{gauch}]}$$

$$\text{and } \ln K_{eq} = \frac{-\Delta G}{RT} = \frac{-900 \text{ cal/mole}}{1.99 \text{ cal/mole K} \times 298 \text{ K}} = 1.52$$

The ratio of K_{eq} is $4.57 \approx 4.6$, which means that about 82% mole $\left(\frac{4.6 \times 100}{5.6}\right)$ of the molecule are in the anti conformation and 18% in the gauch conformation at any one time.

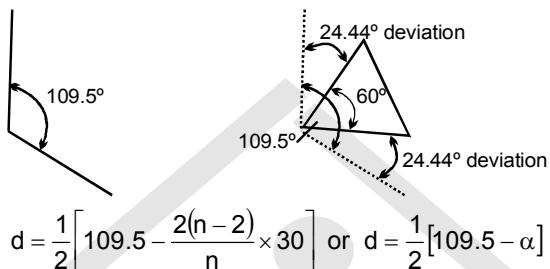
STABILITY OF CYCLOALKANES

Compounds with three and four membered rings are not as stable as compounds with give or six membered rings.

The German chemist Baeyer was the first to suggest that the instability of these small ring compounds was due to angle strain. This theory is known as Baeyer-Strain theory.

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is converted into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule.

Baeyer assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).



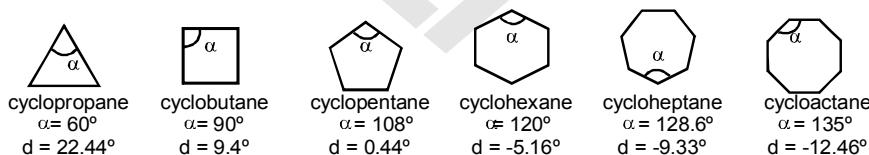
where n = number of carbon-carbon bonds in cycloalkane ring

α = inner bond angle in the cycloalkane ring.

$$\text{Angle strain} \propto d \propto \frac{1}{\text{inner angle}}$$

$$\text{Stability} \propto \frac{1}{d} \propto \text{inner angle} (\alpha)$$

Now let us take the case of three to eight membered cyclic compounds.



The positive and negative values of (d) indicate whether the inner angle is less than or more than the normal tetrahedral value.

Baeyer thus predicted that a five membered ring compound would be the most stable. He predicted that six membered ring compounds would be less stable and as cyclic compound became larger than five membered ring they would become less and less stable.

Contrary to what Baeyer predicted, however, cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of side increase. Thus Baeyer strain theory is applicable only to **cyclopropane, cyclobutane and cyclopentane**.

The mistake that Baeyer made was to assume that all cyclic compounds are planar. In real sense only cyclopropane is planar and other cycloalkanes are not planar. Cyclic compounds **twist** and **bend** in

order to achieve a final structure that minimises the three different kinds of strain that can destabilise a cyclic compound.

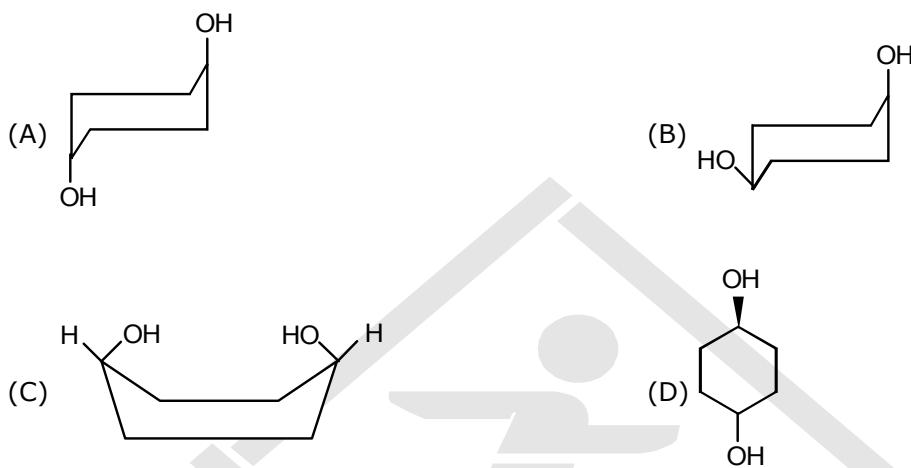
1. **Angle strain** is the strain that results when the bond angle is different from desired tetrahedral bond angle of 109.5° .
2. **Torsional strain** is caused by repulsion of the bonding electrons of one substituent with bonding electrons of a nearby substituent.
3. **Steric strain** is caused by atoms or groups of atoms approaching each other too closely.

Ex.47 According baeyer-strain theory which compound has minimum angle strain?

(A) n-butane (B) cyclopentane (C) cyclopropane (D) cyclohexane

Sol. (B)

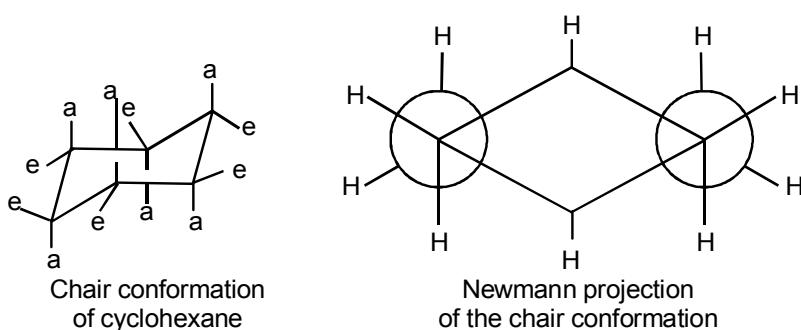
Ex.48 Which form of trans 1,4-cyclohexane diol is most stable?



Sol. (C)

CONFORMATION OF CYCLOHEXANE

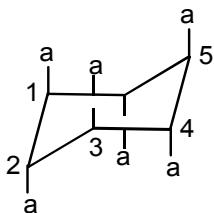
Despite Baeyer's prediction that give-membered cyclic compound would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation**. In a chair conformation of cyclohexane all bond angles are 111° which is very close to the 109.5° and all the adjacent carbon-hydrogen bonds are staggered.



- ⇒ Each carbon in chair conformation has an axial bond and an equatorial bond.
- ⇒ Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.

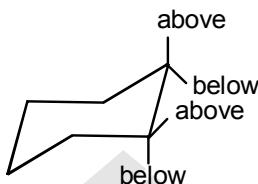
⇒ If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus

C - 1 , C - 3 and C - 5 axial bonds are above
C - 1 , C - 4 and C - 6 axial bonds are below



⇒ Thus C - 1 axial and C - 2 axial are trans to each other. Similarly C - 1 and C - 5 axials are cis to each other.

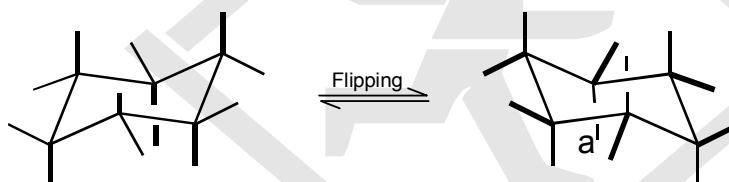
⇒ If axial bond on carbon - I will be above the plane then equatorial bond on this carbon will be below the plane.



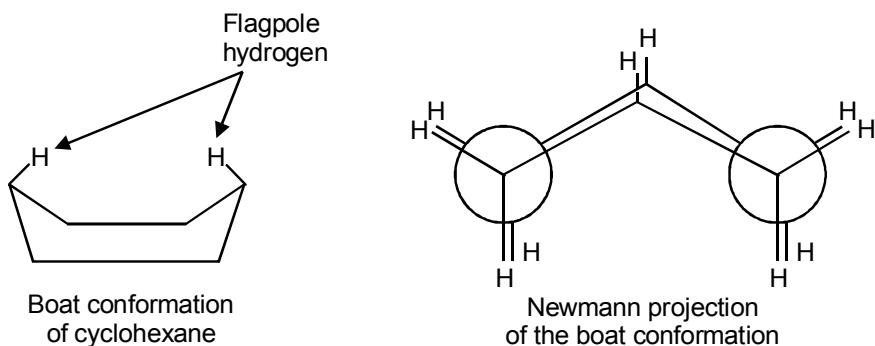
(i) Thus C - 1 equatorial and C - 2 equatorial will be cis

(ii) C - 1 axial and C-2 equatorial will be cis

⇒ As a result of rotation about carbon-carbon single bonds cyclohexane rapidly interconverts between two stable chair conformations. This interconversion is known as ring-flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.



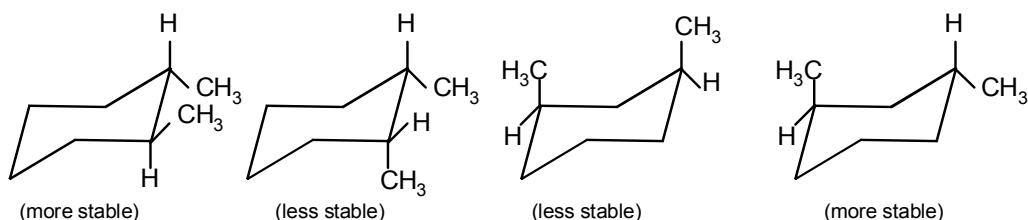
⇒ Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the conformation is less stable than the chair conformation by 11 Kcal/mole. Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.



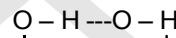
The boat conformation is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 \AA apart but the van der Waal's radii is 2.4 \AA . The flagpole hydrogens are also known as trans nuclear hydrogens.

When one hydrogen of cyclohexane is placed by a larger atom or group, crowding occurs. The most

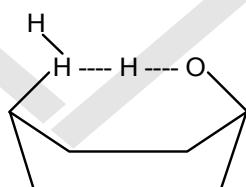
sever crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting repulsive interaction is called 1,3-diaxial interaction. This causes steric strain in the molecule. Thus, monosubstituted cyclohexane will assume chair conformation in which the substituent occupies an equatorial position. Similarly in disubstituted cyclohexanes the chair conformation containing both the substituents in equatorial positions will be the preferred conformation. In general, the conformation with bulkier substituent in an equatorial position will be the preferred conformation. For examples:



cis 1,3-cyclohexanediol has shown to have diaxial rather than the diequatorial orientation. This is because of the stabilisation orientation. This is because of the stabilisation of the diaxial form by intramolecular hydrogen bonding which is not possible in the diequatorial form.



The preferred conformation of the cyclohexane ring is the chair form, but when intramolecular hydrogen bonding is possible between groups in 1 and 4 positions the molecule assumes a boat conformation rather than the chair conformation in which this hydrogen bonding is not possible.



SOME IMPORTANT TERMINOLOGY

Asymmetric carbon : The carbon which is attached with four different groups of atoms is called asymmetric carbon.

Asymmetric molecule : If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.

Achiral molecule : A molecule that is superimposable on its mirror image. Achiral molecules lack handedness and are incapable of existing as a pair of enantiomers.

Axial bond : The six bonds of a cyclohexane ring (below) that are perpendicular to the general plane of the ring, and that alternate up and down around the ring.

Boat conformation : A conformation of cyclohexane that resembles a boat and that has eclipsed bonds along its two sides.

Chair conformation : The all-staggered conformation of cyclohexane that has no angle strain or torsional strain and is therefore, the lowest energy conformation.

Chiral molecule : A molecule that is not superimposable on its mirror image. Chiral molecules have handedness and are capable of existing as a pair of enantiomers.

Chirality : The property of having handedness.

Configuration : The particular arrangement of atoms (or groups) in space that is characteristic of a given stereoisomer.

Conformatoin : A particular temporary orientation of a molecule that results from rotations about its single bonds.

Conformational analysis : An analysis of the energy changes that a molecule undergoes as its groups undergo rotation (sometimes only partial) about the single bonds that join them.

Conformer : A particular staggered conformation of a molecule.

Connectivity : The sequence, or order, in which the atoms of a molecule are attached to each other.

Diastereomers : Stereoisomers that are not mirror images of each other.

Dextrorotatory : Those substances which rotate the plane of polarisation of light towards right are called dextrorotatory. Currently, dextro and laevo rotations are represented by algebraic signs of (+) and (-) respectively.

Eclipsed conformation : A temporary orientation of groups around two atoms joined by a single bond such that the groups directly oppose each other.

Enantiomers : Stereoisomers that are mirror images of each other. enantiomers rotate the plane of polarised light to the same extent but in opposite direction.

Equatorial bond : The six bonds of a cyclohexane ring that lie generally around the "equator" of the molecule.

Levorotatory : A compound that rotates planepolarized light in a counterclockwise direction.

Meso compound : An optically inactive compound whose molecules are achiral even though they contain tetrahedral atoms with four different attached groups. A meso-compound is optically inactive due to internal compensation.

Optically active substances : Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solution are called optically active substances. This phenomenon is called optical activity.

Plane of symmetry : An imaginary plane that bisects a molecule in a way such that the two halves of the molecule are mirror images of each other. Any molecule with a plane of symmetry will be achiral.

Plane-polarized light : Ordinary light in which the oscillations of the electrical field occur only in one plane. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.

Polarimeter : A device used for measuring optical activity.

(R-S) System : A method for designating the configuration of tetrahedral stereogenic centres.

Racemic form (racemate or racemic mixture) : An equimolar mixture of enantiomers. A racemic mixture is optically inactive due to external compensation.

Racemisation : The process of conversion of an enantiomer into racemic mixture is known as an racemisation.

Retention : If in an optically active molecule that relative configuration of the atoms groups around a chiral centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

Relative configuration : The relationship between the configuration of two chiral molecules. Molecules are said to have the same relative configuration when similar or identical groups in each occupy the same position in space. The configuration of molecules can be related to each other through reactions of known stereochemistry, for example through reactions that cause no bonds to a stereogenic center to be broken.

Resolution : The process by which the enantiomers of a recemic form are separated.

Ring flip : The change in a cyclohexane ring (resulting from partial bond rotations) that converts one ring conformation to another. A chair-chair ring flip converts any equatorial substituent to an axial substituent and vice versa.

Ring strain : The increased potential energy of the cyclic form of a molecule (usually measured by heats of combustion) When compared to its acyclic form.

Specific rotation : Specific rotation is defined as the number of degrees of rotation observed when the concentration of optically active substance is 1 g cm^{-3} and length of polarimeter tube is 1 decimetre (dm) for D-line of sodium vapour lamp at 25°C .

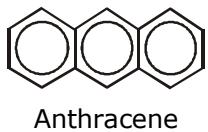
Stereogenic center : An atom bearing group of such nature that an interchange of any two groups will produce a stereoisomer.

Steric hindrance : An effect on relative reaction rates caused when the spatial arrangement of atoms or groups at or near the reacting site hinders or retards a reaction.

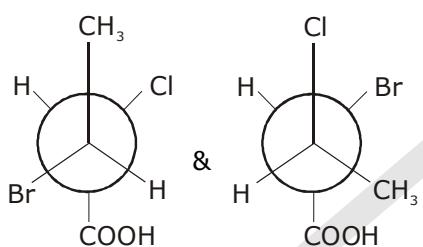
Torsional strain : The strain associated with an eclipsed conformation of a molecule; it is caused by repulsions between the aligned electron pairs of the eclipsed bonds.

Sol.

11. How many planes (pos) are presents in Anthracene



(A) 1 (B) 2 (C) 3 (D) 6

Sol.**12.**

(A) Comformers
(C) Enantiomers

Sol.

(B) Diastereomers
(D) Position isomers

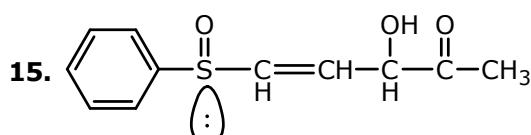
13. Geometrical isomers can be

(A) Diastereomers or Enantiomers
(B) Structural isomers
(C) Inter convertible at room temperature.
(D) none of these

Sol.

14. Phenol and benzyl alcohol are

(A) functional isomers
(B) Homologous
(C) position isomers
(D) none of these

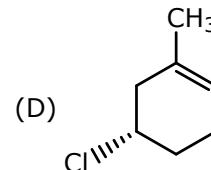
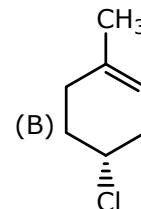
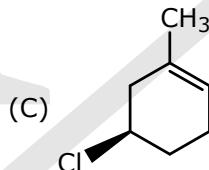
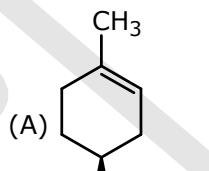
Sol.

Number of chiral centers are:

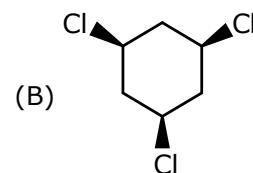
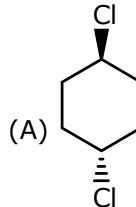
(A) 1 (B) 2 (C) 3 (D) 4

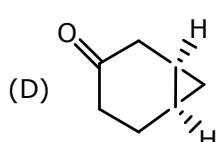
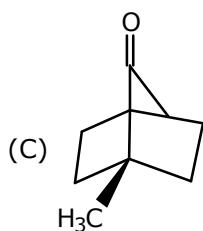
Sol.

16. Which of the following compounds is (S)-4-chloro-1-methylcyclohexene?

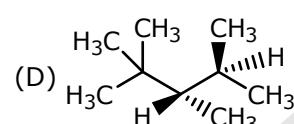
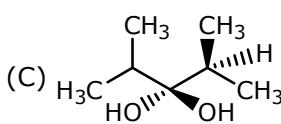
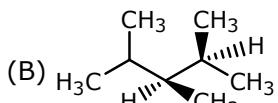
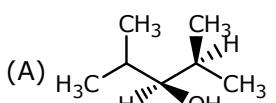
**Sol.**

17. Which of the following compounds has two stereogenic centers (asymmetric carbons)?



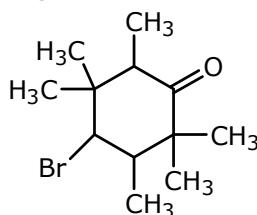


18. Which of the following structures represents a chiral compound?



Sol.

19. Examine the compound on the right. How many stereoisomers having this constitution are possible?



(A) 2 (B) 4 (C) 6 (D) 8

Sol.

20. Which of the following heptanols are chiral 1-heptanol, 2-heptanol, 3-heptanol, 4-heptanol.

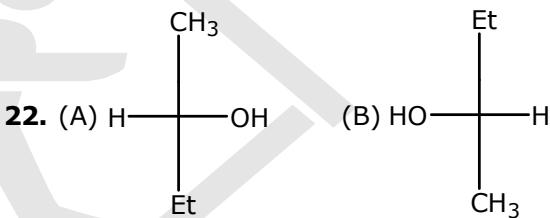
(A) All are chiral
 (B) 2-heptanol and 3-heptanol
 (C) 2-heptanol, 3-heptanol & 4-heptanol
 (D) 3-heptanol and 4-heptanol

Sol.

21. Which of the following will exhibit geometrical isomerism?

(A) 1-phenyl-2-butene
 (B) 3-phenyl-1-butene
 (C) 2-phenyl-1-butene
 (D) 1, 1-diphenyl-1-propene

Sol.

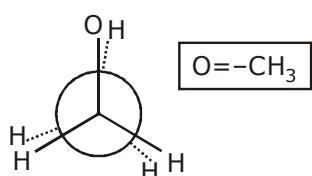


Relation between given pair is

(A) Enantiomer (B) Diastereomer
 (C) Identical (D) Structural isomer

Sol.

23. Following eclipsed form of propane is repeated after rotation of



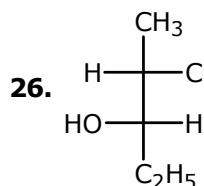
(A) 45° (B) 90° (C) 120° (D) 180°

Sol.

Sol.

25. The number of isomers of C_5H_{10} is
 (A) 10 (B) 11 (C) 12

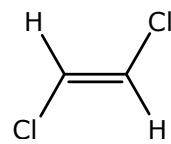
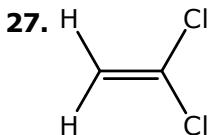
Sol.



configuration is called.

- (A) (2S, 3S)-2-chloro-3-hydroxypentane
- (B) (2S, 3R)-2-chloro-3-hydroxypentane
- (C) (2R, 3R)-2-chloro-3-hydroxypentane
- (D) (2R, 3S)-2-chloro-3-hydroxypentane

()



The above compounds differ in

(A) configuration (B) conformation
(C) structure (D) chirality

Sol.

28. The compound $C_2H_5OC_2H_5$ and $CH_3OCH_2CH_2CH_3$ are
(A) enantiomers
(B) geometrical isomers
(C) metamers
(D) conformational isomers

Sol.

Sol.

(3)

EXERCISE – II**JEE ADVANCED (OBJECTIVE)**

1. A pure sample of 2-chlorobutane shows rotation of PPL by 30° in standard conditions. When above sample is made impure by mixing its opposite form, so that the composition of the mixture become 87.5% d-form and 12.5% l-form, then what will be the observed rotation for the mixture.

(A) -22.5° (B) $+22.5^\circ$ (C) $+7.5^\circ$ (D) -7.5°

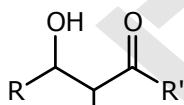
Sol.

2. When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution rotates the PPL by 30° . Calculate the angle of rotation & specific angle of rotation if above solution diluted to 1 Litre.

(A) 16° & 36° (B) 6° & 30°
 (C) 3° & 30° (D) 6° & 36°

Sol.

3. In the given following compound find out the pair of enantiomers and diastereomers



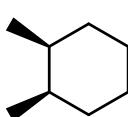
(A) 2, 2 (B) 2, 4 (C) 4, 4 (D) 4, 2

Sol.

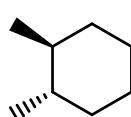
4. The molecule(s) that exist as meso structure(s)



(K)
 (A) only M
 (C) only L



(L)
 (B) both K and L
 (D) only K



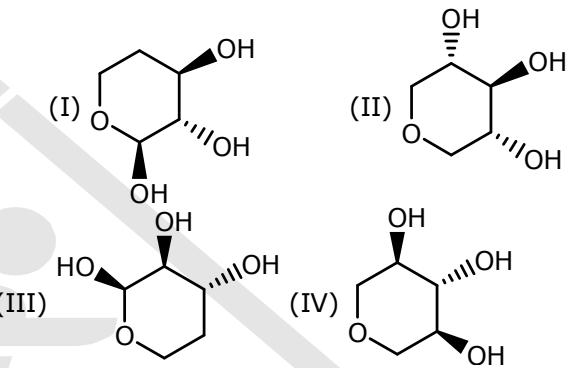
Sol.

5. Among the following, a pair of resolvable configurational enantiomers is given by

(A) cis-1, 2-dimethylcyclohexane
 (B) cis-1, 3-dimethylcyclohexane
 (C) cis-1, 4-dimethylcyclohexane
 (D) trans-1, 3-dimethylcyclohexane

Sol.

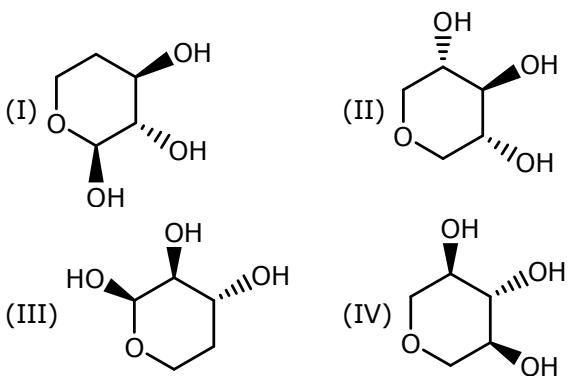
6. Which two of the following compounds are identical?



(A) I & II (B) II & IV (C) III & IV (D) I & III

Sol.

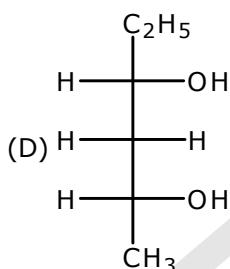
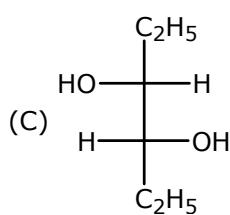
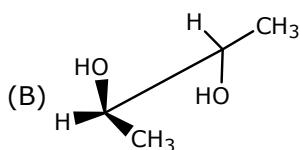
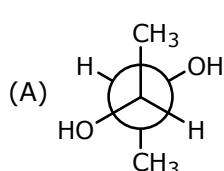
7. Which two of the following compounds are diasteromers?



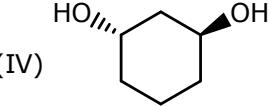
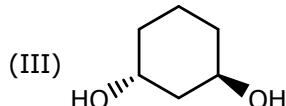
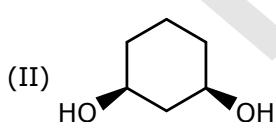
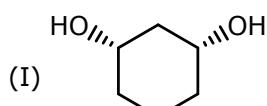
(A) I & II (B) II & IV (C) III & IV (D) I & III

Sol.

8. Which of the following is properly classified as a meso compound?

**Sol.**

9. Which two of the following compounds represents a pair of enantiomers?

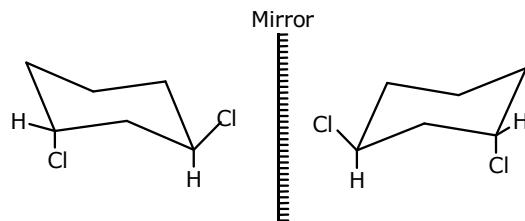


(A) I & II (B) II & III (C) III & IV (D) II & IV

Sol.

10. The drawing on the right shows that trans-1, 3-dichlorocyclohexane is chiral.

Efforts to resolve this compound fail. Why?



(A) the cis and trans isomers rapidly interconvert.
 (B) the compound is actually a meso structure.
 (C) the chair conformers rapidly interconvert producing a racemic mixture.
 (D) method for resolving alkyl chlorides are not available.

Sol.

11. How many stereoisomers of $(CH_3)_2CHCH = CHCH_2CH(OH)CH_2Br$ are possible?

(A) 2 (B) 3 (C) 4 (D) 5

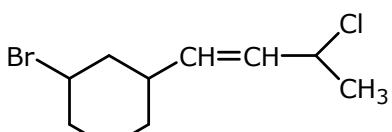
Sol.

12. What common symmetry of elements if any are found in the stable chair conformer of trans-1, 2-dichlorocyclohexane?

(A) A single mirror plane and a C_2 rotational axis.
 (B) A single mirror plane & C_3 rotational axis.
 (C) Two orthogonal mirror planes and a C_2 rotational axis.
 (D) A single C_2 rotational axis but no mirror plane.

Sol.

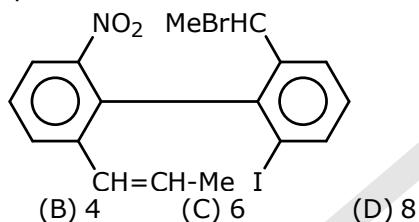
13. How many stereoisomer are possible for the following molecule ?



(A) 4 (B) 8 (C) 16 (D) 32

Sol.

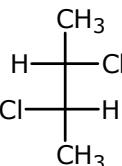
14. How many stereoisomers are possible for the following compound ?



(A) 2 (B) 4 (C) 6 (D) 8

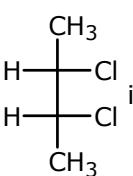
Sol.

15. Optical rotation produced by



is 36° then

that product by



(A) -36° (B) 0°
(C) +36° (D) unpredictable

Sol.

19. Number of structural isomers of compound having molecular formula C_4H_7Cl .

(A) 4 (B) 8 (C) 12 (D) 16

16. $CH_3-CH_2-CH_2-CH_2$ and $CH_3-C(CH_3)-CH_3$ are

(A) chain isomers (B) positional isomers
(C) both (D) none

Sol.

17. Dextrorotatory α -pinene has a specific rotation $[\alpha]_D^{20} = +51.3^\circ$. A sample of α -pinene containing both the enantiomers was found to have a specific rotation value $[\alpha]_D^{20} = +30.8^\circ$. The percentages of the (+) and (-) enantiomers present in the sample are, respectively.

(A) 70% and 30% (B) 80% and 20%
(C) 20% and 80% (D) 60% and 40%

Sol.

18. (+)-mandelic acid has a specific rotation of 158° . What would be the observed specific rotation of a mixture of 25% (-)-mandelic acid and 75% (+)-mandelic acid ?

(A) $+118.5^\circ$ (B) -118.5°
(C) -79° (D) $+79^\circ$

Sol.

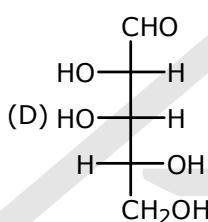
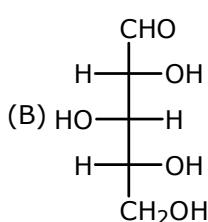
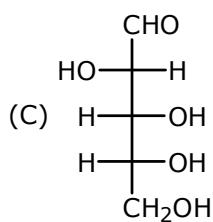
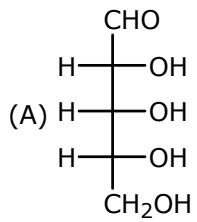
Sol.

22. Which of the following statements is true for a pair of diastereomers ?

- they will have identical physical properties.
- they will have specific rotations of opposite sign
- they will have identical chemical properties (e.g. reactivity)
- they will have different physical properties.

Sol.

20. Which of the following sugars has the configuration (2S 3R, 4R) ?

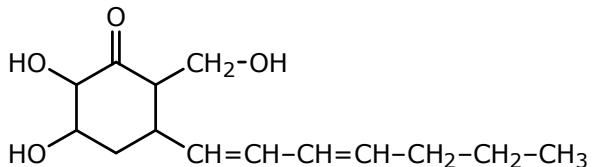
**Sol.**

21. Which of the following statements must be true for two pure chiral isomers ?

- they must be enantiomers
- they must be diastereomers
- they must be stereoisomers
- they must be optically active

Sol.

23. How many stereoisomer may have this natural occurring compound.



(A) 8 (B) 16 (C) 64 (D) 128

Sol.

24. An optically pure compound X gave an $[\alpha]_D^{25} = +20.0^\circ$. A mixture of X and its enantiomer Y gave $[\alpha]_D^{25} = +10^\circ$. The ratio of X to Y in the mixture is

- 2 : 1
- 1 : 3
- 3 : 1
- 1 : 2

Sol.

25. Molecular formula $C_3H_6Br_2$ can have (including stereoisomers):

- Two gem dibromide
- One vic dibromide
- Two tertiary dibromo alkane
- Two secondary dibromo alkane

Sol.**26.** Mesotartaric acid and d-tartaric acid are

(A) position isomers (B) enantiomers
 (C) diastereomers (D) racemic mixture

Sol.**27.** The number of isomers of $C_3H_5Br_3$ (including stereoisomers)

(A) 4 (B) 5 (C) 6 (D) 7

Sol.**28.** The number of optically active compounds in the isomers of C_4H_9Br is

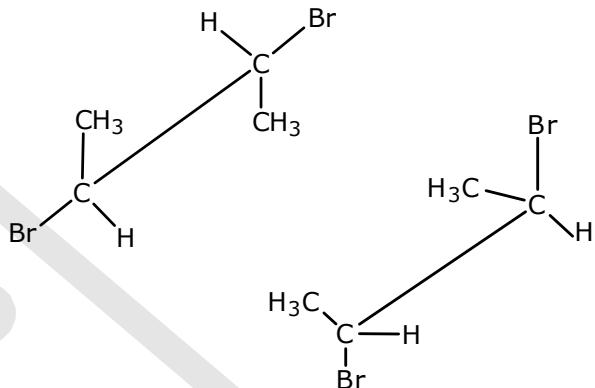
(A) 1 (B) 2 (C) 3 (D) 4

Sol.**29.** The preferred conformation of trans-1, 2-dibromocyclohexane is:

(A) diaxial (B) diequatorial
 (C) axial/equatorial (D) neither A, B nor C

Sol.**30.** How many stereoisomers of the following molecule are possible? $HOOC.CH=C=CH.COOH$

(A) Two optical isomers
 (B) Two geometrical isomers
 (C) Two optical & two geometrical isomers
 (D) None

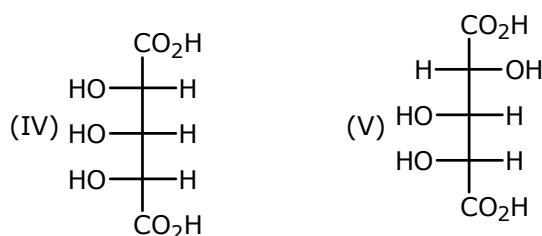
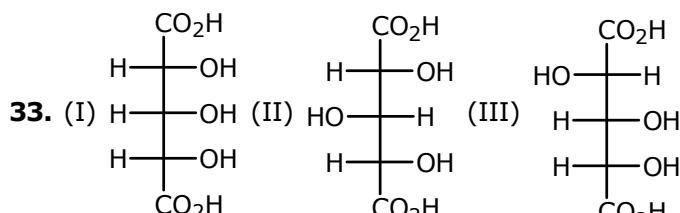
Sol.**31.** The structures shown here are related as being

(A) conformers (B) enantiomorphs
 (C) geometrical isomers (D) diastereoisomers

Sol.**32.** Which of the following cannot be written in an isomeric form?

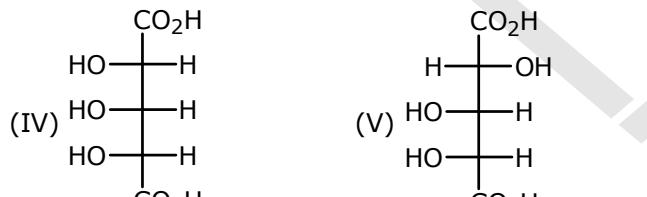
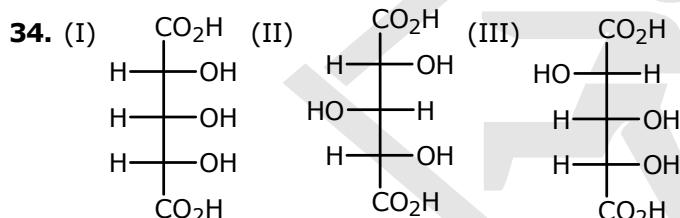
(A) $CH_3 - CH(OH) - CH_2 - CH_3$
 (B) $CH_3 - CHO$
 (C) $CH_2 = CH - Cl$
 (D) $Cl - CH_2CH_2 - Cl$

Sol.



Which of the above formula represent identical compounds?

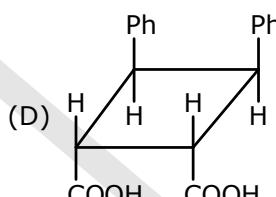
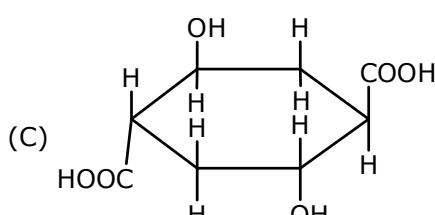
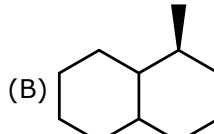
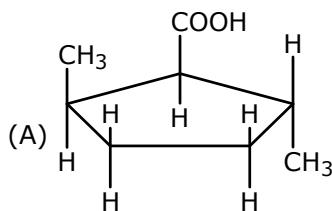
Sol.



which of the above compounds are in enantiomers

()

35. Which species exhibits a plane of symmetry ?



Sol.

36. Number of possible 3D-isomers (Stereoisomer) of glucose are

(A) 10 (B) 14 (C) 16 (D) 20

()

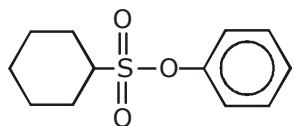
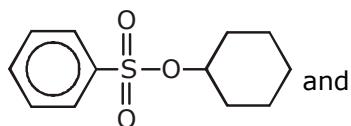
37. Which of the following, compounds displays geometrical isomerism ?

(A) $\text{CH}_2 = \text{CHBr}$ (B) $\text{CH}_2 = \text{CBr}_2$
 (C) $\text{ClCH} = \text{CHBr}$ (D) $\text{Br}_2\text{C} = \text{CCl}_2$

Sol.

Sol.

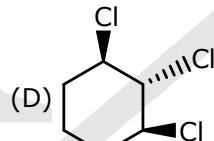
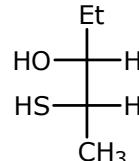
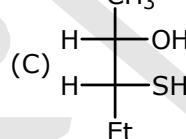
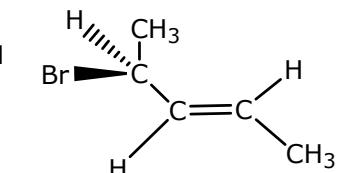
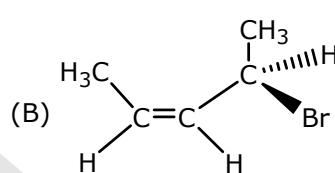
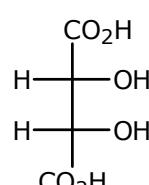
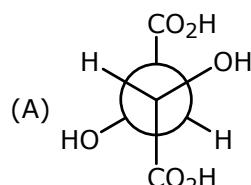
44. Given compound show which type of isomerism?



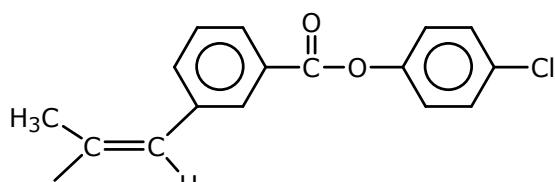
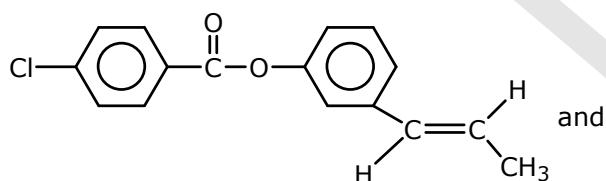
- (A) Chain isomerism
- (B) Positional isomerism
- (C) Metamerism
- (D) Functional group isomerism

Sol.

46. Which of following pair is Diastereomers:



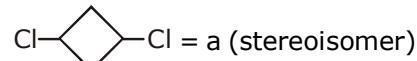
45. Shows which type of isomerism



- (A) Functional group isomerism
- (B) Geometrical isomerism
- (C) Metamerism
- (D) Position isomerism

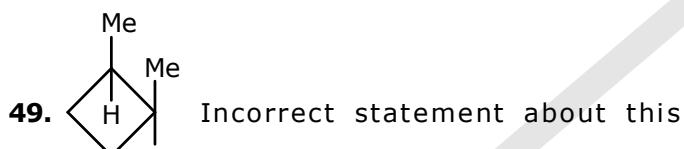
Sol.

47. Sum of stereoisomer in the given compound (a) and (b) are:

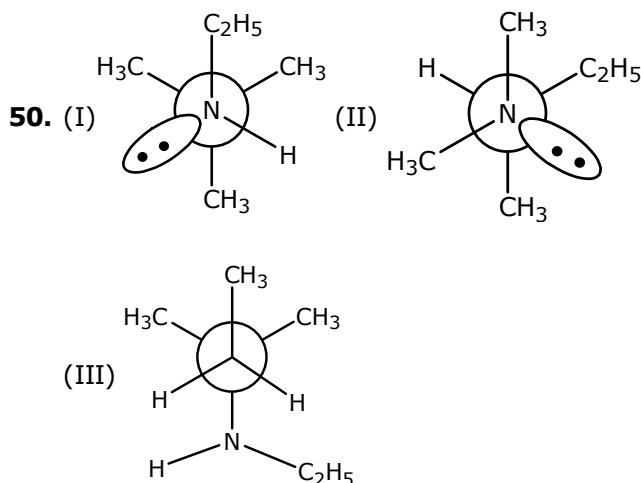


Sol.

equilibrium constant for above reaction is:

(A) $K = 1$ (B) $K > 1$ (C) $K < 1$ (D) $K = 0$ **Sol.**

(A) it shows geometrical isomerism
 (B) it posses centre of symmetry
 (C) it posses plane of symmetry
 (D) it shows optical isomerism

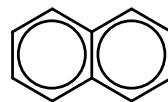
Sol.

Which of the following statement is correct ?

(A) I & II are conformational isomers while II & III are functional isomers
 (B) I & II are functional isomers while II & III are conformational isomers
 (C) I & II are functional isomers while I & III are conformational isomers
 (D) None of these

Sol.

51. How many planes are presents in naphthalene

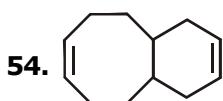


Naphthalene

(A) 1 (B) 2 (C) 3 (D) 6**Sol.**52. Total number of optically active alkyne possible from molecular formula $C_3FClBrI$ (A) 2 (B) 4 (C) 6 (D) 8**Sol.**

53. Total number of geometrical isomer of given compound will be

(A) 2 (B) 4 (C) 6 (D) 8**Sol.**



Number of geometrical isomer of given compound will be :

(A) 2 (B) 3 (C) 4 (D) 5

Sol.

55. The number of stereoisomers obtained by bromination of cis-2-butene is

(A) 1 (B) 2 (C) 3 (D) 4

Sol.

56. The number of stereoisomers obtained by reaction cis-2-butene with bromine in the presence of water is :

(A) 1 (B) 2 (C) 3 (D) 4

Sol.

57. The number of stereoisomers obtained by bromination of trans-2-butene is :

(A) 1 (B) 2 (C) 3 (D) 4

Sol.

58. The number of stereoisomers obtained by bromination of 1-butene is :

(A) 1 (B) 2 (C) 3 (D) 4

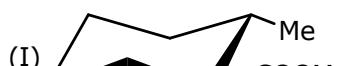
Sol.

59. Isobutene + Br₂ → Number of possible products

(A) 1 (B) 2 (C) 3 (D) 4

Sol.

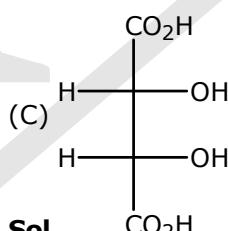
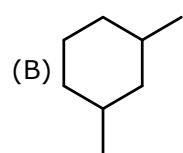
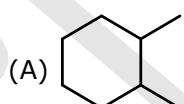
60. In which of the following molecule show chirality.



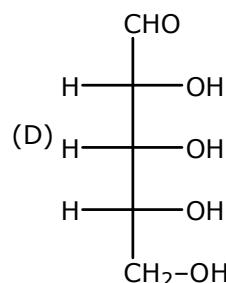
(A) I is trans & chiral (B) II is trans & chiral
(C) I is cis & chiral (D) II is trans & achiral

Sol.

61. Total number of stereoisomer is odd number for



Sol.



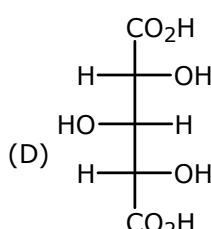
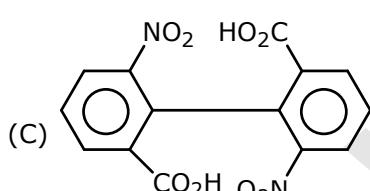
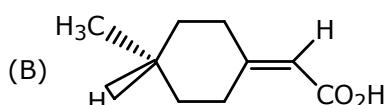
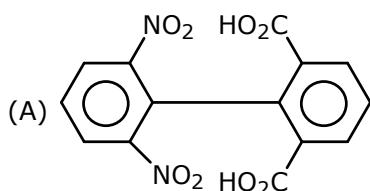
62. **Statement-1 :** This compound will show geometrical isomerism.

Statement-2 : Terminal carbon groups are perpendicular to each other.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT correct explanation for statement-1
 (C) Statement-1 is true, statement-2 is false
 (D) Statement-1 is false, statement-2 is true

Sol.

63. Which of the following compounds is optically active ?

**Sol.**

64. $C_4H_6O_2$ does represent

(A) A diketone
 (B) A compound with two aldehyde
 (C) An alkenoic acid
 (D) An alkanoic acid

Sol.

65. Which of the following statement is/are not correct?

(A) Metamerism belongs to the category of structural isomerism
 (B) Tautomeric structures are the resonating structures of a molecule
 (C) Keto form is always more stable than the enol form
 (D) Geometrical isomerism is shown only by alkenes.

Sol.

66. Which of the following statements is/are correct ?

(A) A meso compound has chiral centres but exhibits no optical activity.
 (B) A meso compound has no chiral centres and thus are optically inactive.
 (C) A meso compound has molecules which are superimposable on their mirror images even though they contain chiral centres.
 (D) A meso compound is optically inactive because the rotation caused by any molecule is cancelled by an equal and opposite rotation caused by another molecule that is the mirror image of the first.

Sol.

67. Which of the following statements is/are not correct D-(+) glyceraldehyde ?

(A) The symbol D indicates the dextrorotatory natures of the compound
 (B) The sign (+) indicates the dextrorotatory nature

of the compound

(C) The symbol D indicates that hydrogen atom lies left to the chiral centre in the Fischer projection diagram.

(D) The symbol D indicates that hydrogen atom lies right to the chiral centre in the Fischer projection diagram.

Sol.

68. Which of the following compounds is optically active?

(A) 1-Bromobutane (B) 2-Bromobutane
 (C) 1-Bromo-2-methylpropane
 (D) 2-Bromo-2-methylpropane

Sol.

69. Which of the following operations on the Fischer

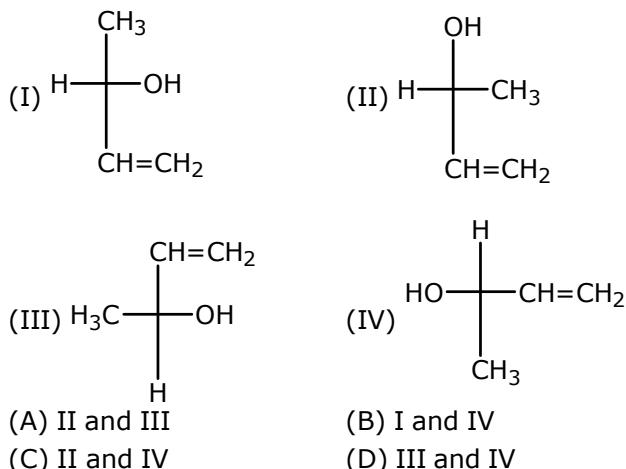
formula $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{C}_2\text{H}_5 \end{array}$ does not change its absolute

configuration

(A) Exchanging groups across the horizontal bond
 (B) Exchanging groups across the vertical bond
 (C) Exchanging groups across the horizontal bond and also across the vertical bond
 (D) Exchanging a vertical and horizontal group.

Sol.

70. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?



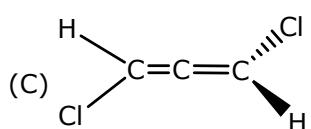
71. Which of the following statements for a meso compound is/are correct?

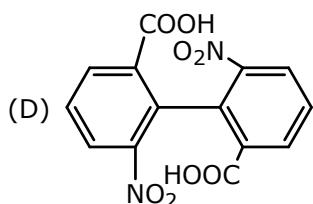
(A) The meso compound has either a plane or a point of symmetry
 (B) The meso compound has at least one pair of similar stereocenters
 (C) The meso compound is achiral
 (D) The meso compound is formed when equal amounts of two enantiomers are mixed

Sol.

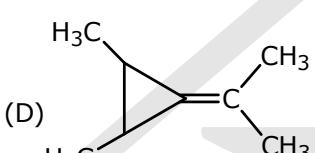
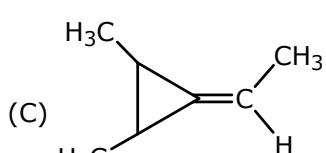
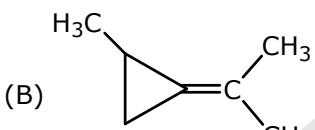
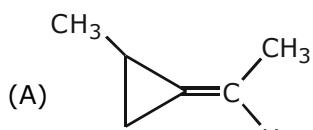
72. Which of the following compounds are optically active?

(A) $\text{CH}_3.\text{CHOH}.\text{CH}_2\text{CH}_3$
 (B) $\text{H}_2\text{C} = \text{CH} . \text{CH}_2.\text{CH} = \text{CH}_2$

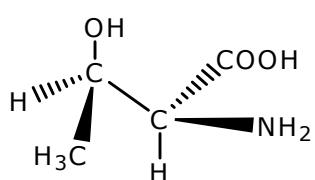
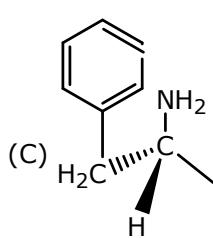
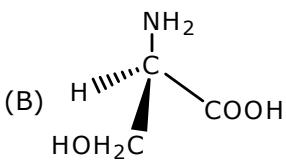
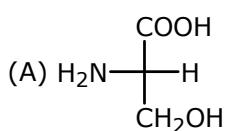


**Sol.**

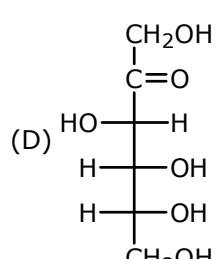
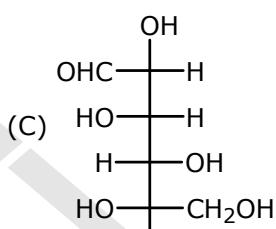
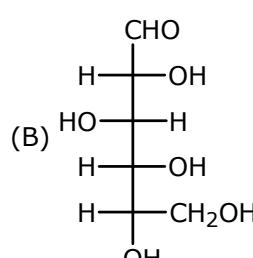
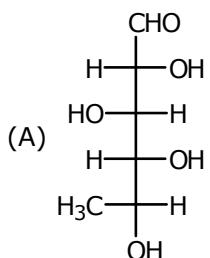
73. Which of the following will show optical isomerism as well as geometrical isomerism.

**Sol.**

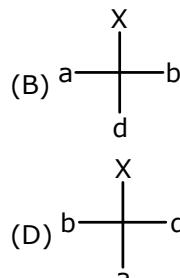
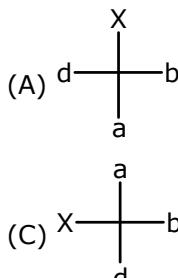
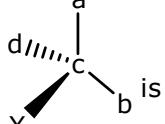
74. Which of the following are correct represents of L-amino acids

**Sol.**

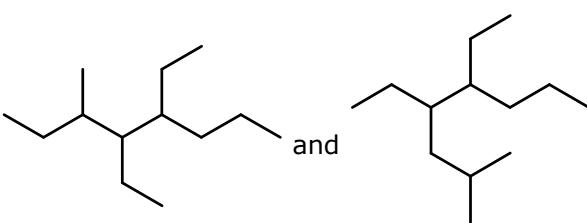
75. Which of the following are D sugars.

**Sol.**

76. The Fischer projection of the molecule as represented in the wedge edge.

**Sol.**

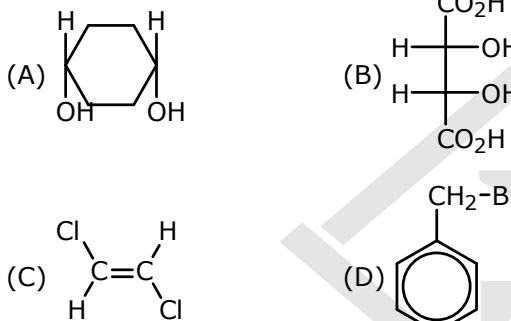
77. Given compound shows which type of isomerism



- (A) Chain isomerism
- (B) Positional isomerism
- (C) Constitutional isomerism
- (D) None

Sol.

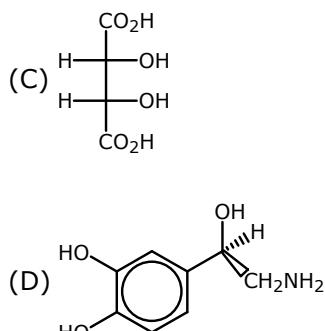
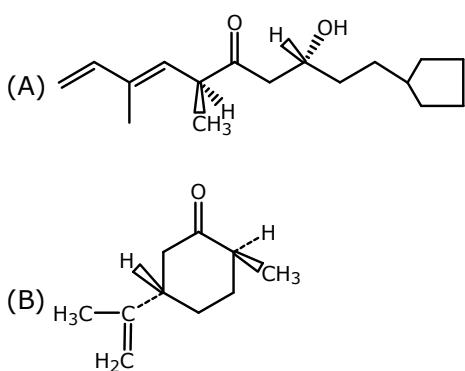
78. Which of following compound having plane of symmetry



Sol.

79. Match the column:

Column-I



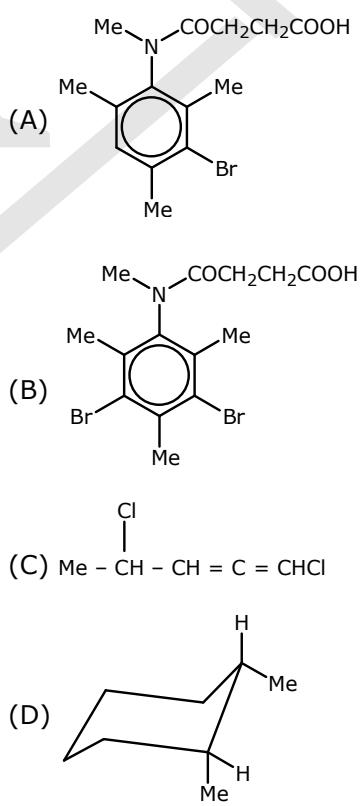
Column-II

- (P) Total number of stereoisomers is odd for structure
- (Q) Total number of stereoisomers is even for the structure
- (R) Odd number of chiral centres
- (S) Even number of chiral centres

Sol.

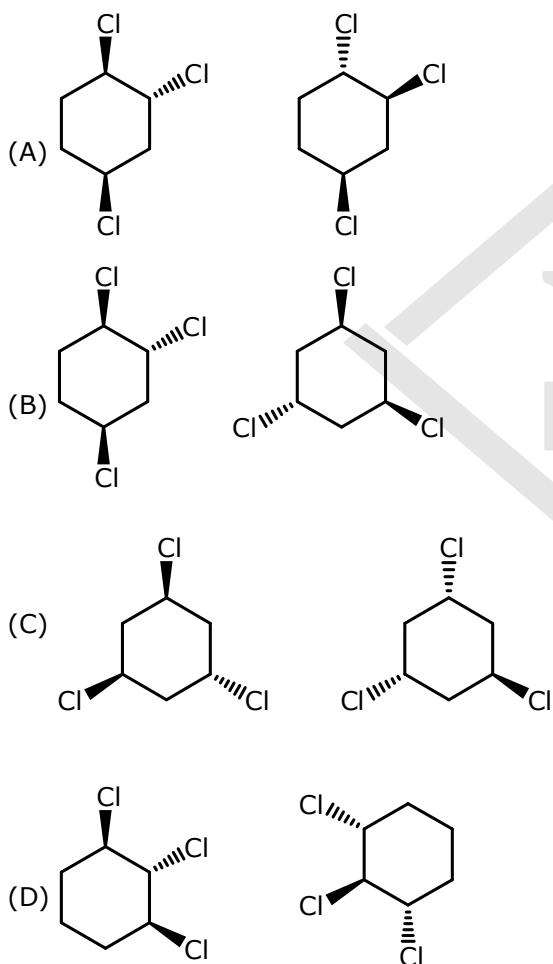
80. Match the column:

Column-I

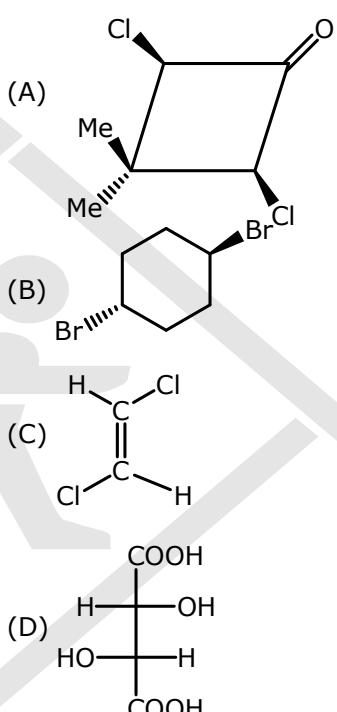


Column-II

(P) Show optical isomerism
 (Q) Show geometrical isomerism
 (R) resolvable
 (S) non-resolvable

Sol.**81. Match the column:****Column-I****Column-II**

(P) Position isomers
 (Q) Enantiomers
 (R) Diastereomers
 (S) Identical

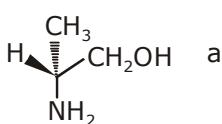
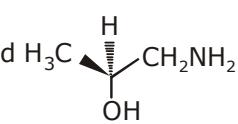
Sol.**82. Match the column :****Column-I****Column-II**

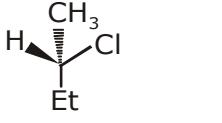
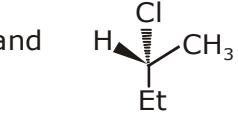
(P) Total number of stereoisomers are odd.
 (Q) Total number of stereocentres are even or have centre of symmetry
 (R) Compounds having plane of symmetry or axis of symmetry
 (S) Compounds have zero dipole in given form.

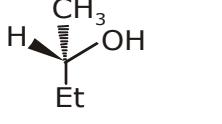
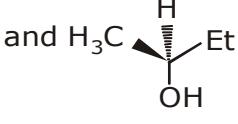
Sol.

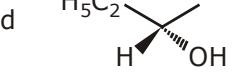
83. Match the column :

Column-I

(A)  and 

(B)  and 

(C)  and 

(D)  and 

Column-II

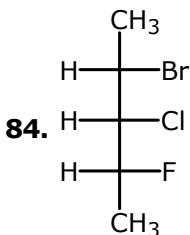
(P) Structural isomer
 (Q) Identical
 (E) Enantiomers
 (S) Diastereomers

Sol.

Paragraph for Questions Nos. 84 to 86

If a molecule contains one carbon atom carrying four different groups it will not have a plane of symmetry and must therefore be chiral. A carbon atom carrying four different groups is a stereogenic or chiral centre.

A structure with a plane of symmetry is achiral and superimposable on its mirror image and cannot exist as two enantiomer. A structure without a plane of symmetry is chiral and not superimposable on its mirror image and can exist as two enantiomer.

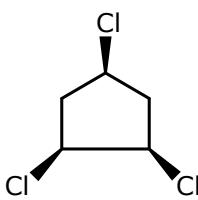


Number of enantiomeric pairs are

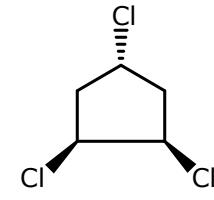
(A) 2 (B) 4 (C) 8 (D) 10

Sol.

85. (a)



(b)

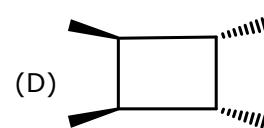
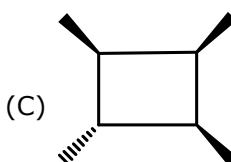
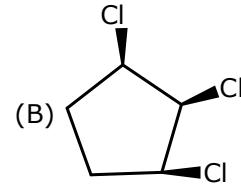
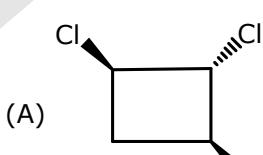


Relation between (a) & (b) is

(A) Enantiomer (B) Diastereomer
 (C) Identical (D) Structural isomer

Sol.

86. Compound has both center of symmetry and P.O.S



Sol.

EXERCISE – III**JEE ADVANCED**

1. What kind of reagent would be needed to resolve a recemic amine, such as 2-aminobutane?

(A) the pure optically active amine to serve as a template for crystallization.

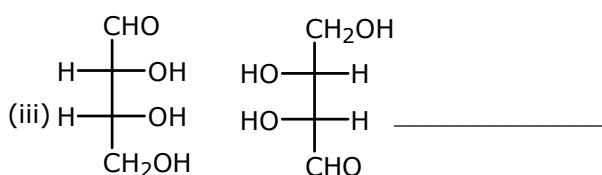
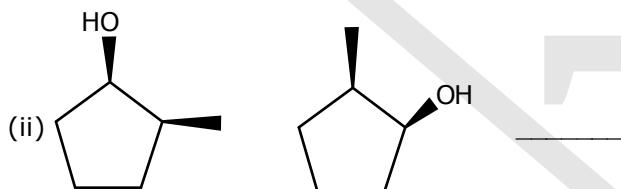
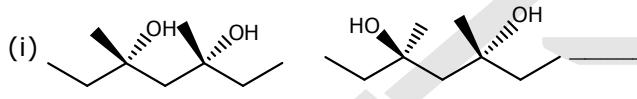
(B) an achiral carboxylic acid to give a recemic mixture of amine salts.

(C) an enantiomerically pure chiral carboxylic acid to give a diastereomeric mixture of amine salts.

(D) a recemic chiral carboxylic acid to give a complete mixture of isomeric amine salts.

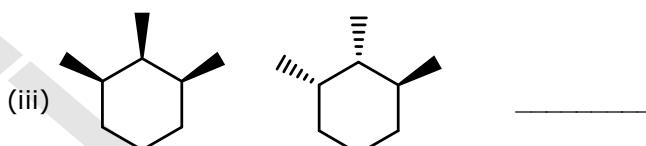
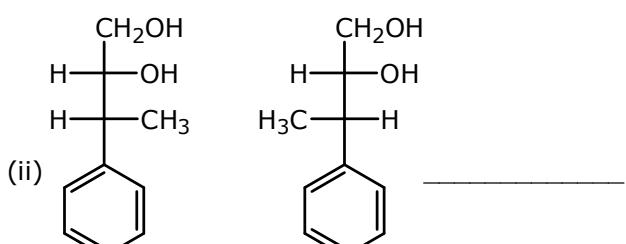
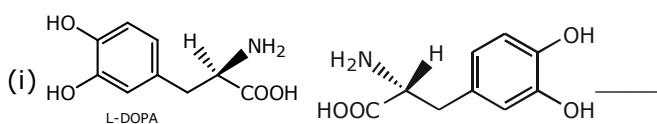
Sol.

2. Determine if the following pairs are identical, isomers, enantiomers, or diastereomers.



Sol.

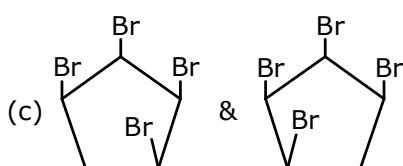
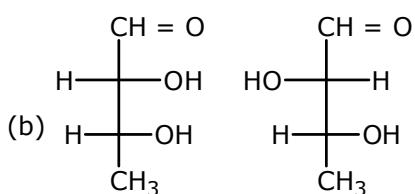
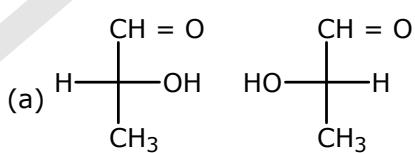
3. Determine if the following pairs are identical, isomers, enantiomers, or diastereomers.



Sol.

4. Classify each of the following pairs of structure as

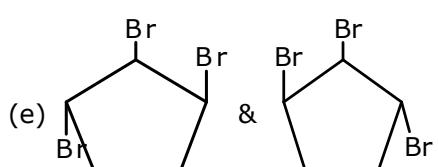
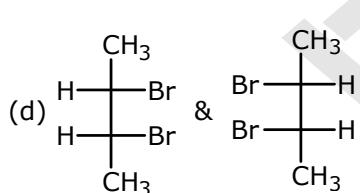
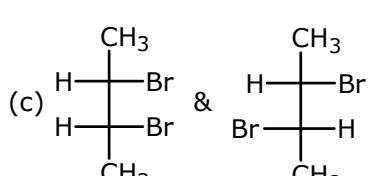
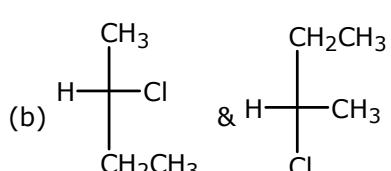
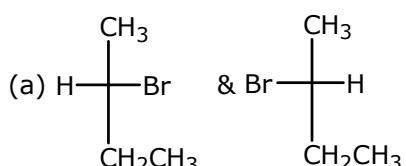
I. Identical E. Enantiomers. D. Diastereomers



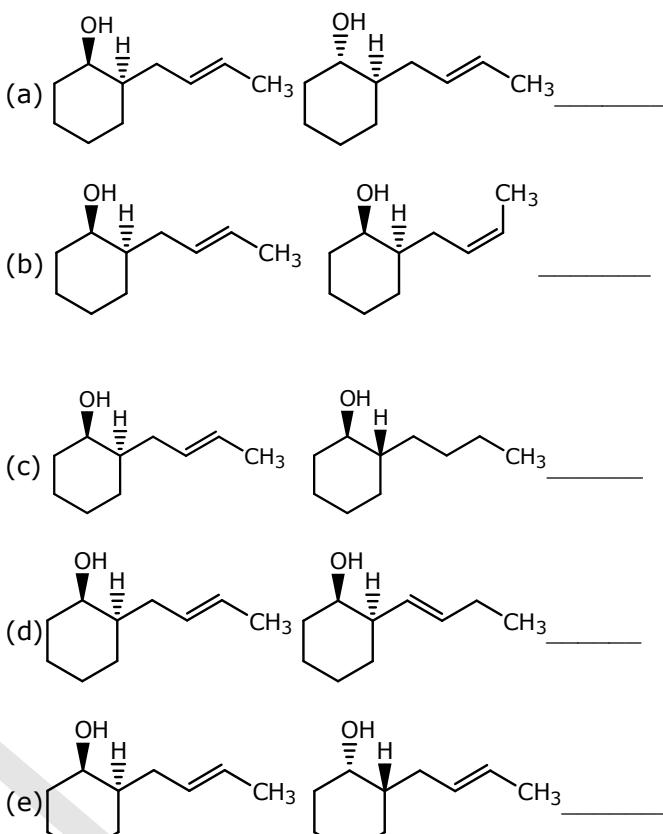
Sol.

5. Classify each of the following pairs of structure (a)-(e) as:

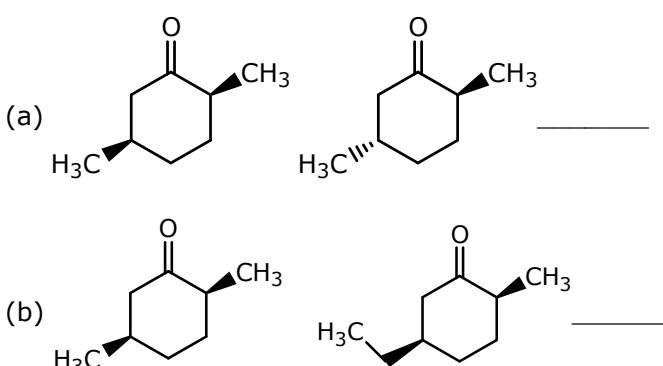
I. Identical E. Enantiomers. D. Diastereomers

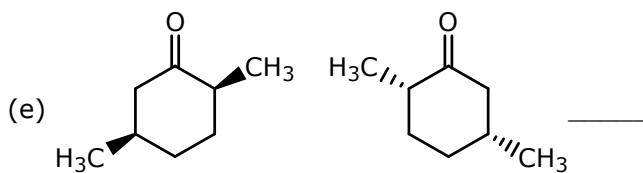
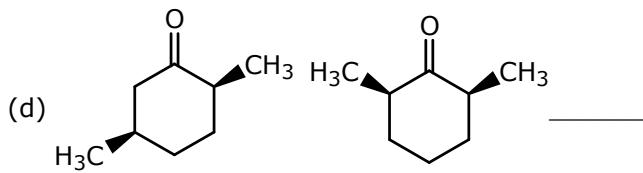
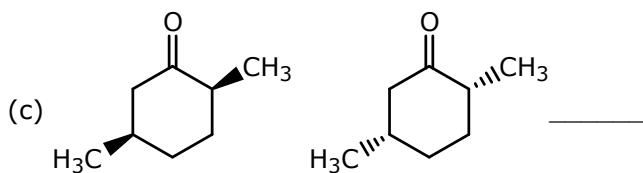
**Sol.**

6. State the relationship between each of the following five (5) pairs of structures (identical, enantiomers, diastereomers, structural isomers, conformational isomers, different compounds that are not isomeric)

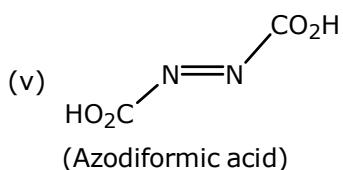
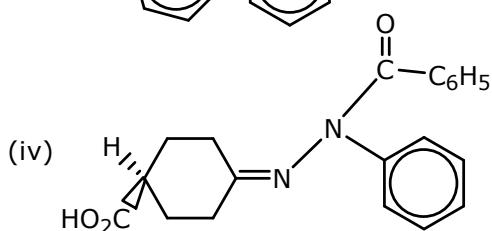
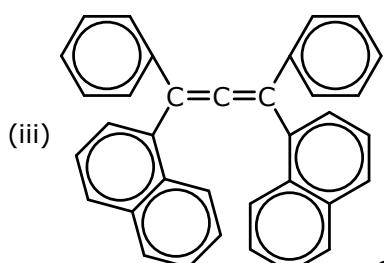
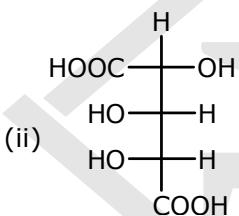
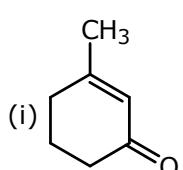
**Sol.**

7. State the relationship between each of the following five (5) pairs of structures (identical, enantiomers, diastereomers, structural isomers, conformational isomers, different compounds that are not isomeric)



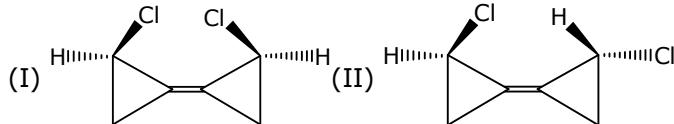


8. Select chiral molecule out of the following list compound



Sol.

9. Discuss the optical activity of the following two compounds and also label them as polar and non polar.

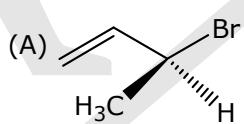


Sol.

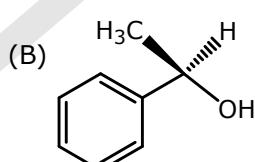
10. (18) Now for some questions about stereochemical relationships.

Column A

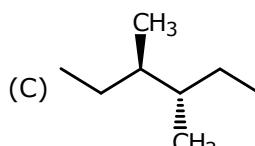
Circle the word (s) in this column that describe the molecules in column A.



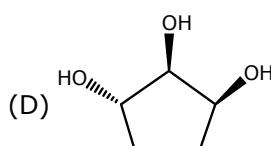
chiral
meso
achiral
none of these



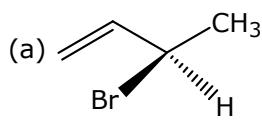
chiral
meso
achiral
none of these



chiral
meso
achiral
none of these

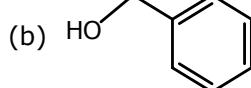


chiral
a
meso
chiral
none of these

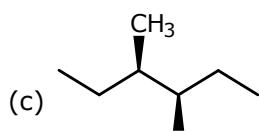
Column B**Circle one word in this column**

that best describes the relationship of the molecules in columns A and B

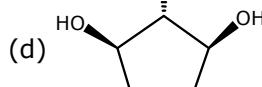
enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these

Sol.

11. A cyclobutandicarboxylic acid exist in two stereoisomeric forms in which one is polar but non-resolvable while other is non-polar but resolvable into enantiomers. Deduce structures of all these compounds.

Sol.

12. How many isomers are possible for nitrophenol ?

Sol.

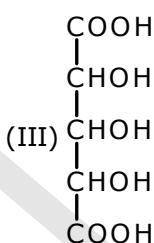
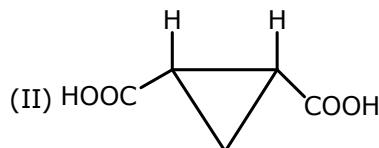
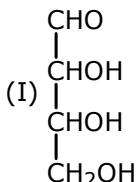
that best describes the relationship of the molecules in columns A and B

enantiomers diastereomers identical none of these

13. A compound with molecular formula $C_4H_{10}O$, can show metamerism, functional isomerism and positional isomerism. Justify the statement.

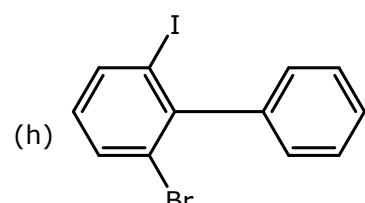
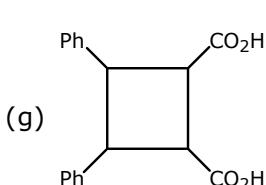
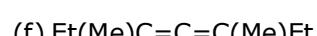
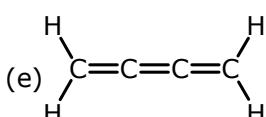
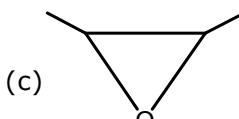
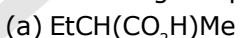
Sol.

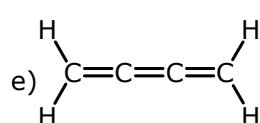
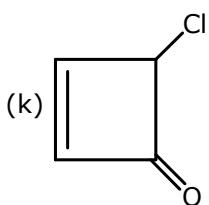
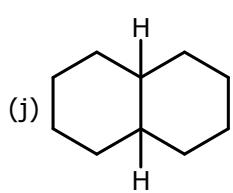
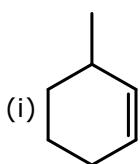
14. Calculate the total number of stereoisomers in the following compounds.



Sol.

15. In what stereoisomeric forms would you expect the following compounds to exist ?





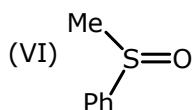
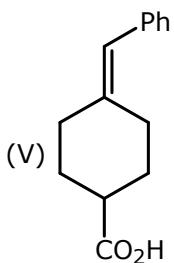
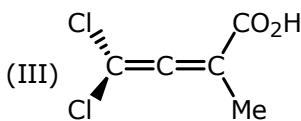
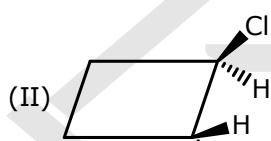
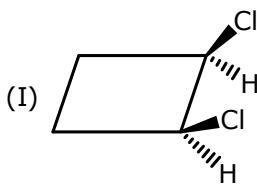
Sol.

17. Considering rotation about the C-3 – C-4 bond of 2-methylhexane

- (a) Draw the Newman projection of the most stable conformer
- (b) Draw the Newman projection of the least stable conformer

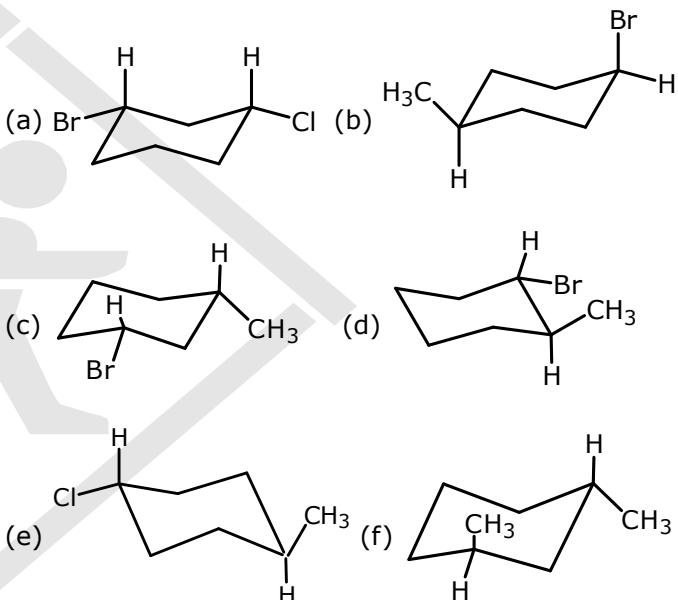
Sol.

16. With reasons, state whether each of the following compounds I to VII is chiral.



Sol.

18. Determine whether each of the following compounds is a cis isomer or a trans isomer.



Sol.

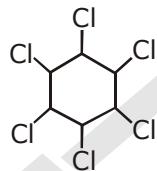
19. An object that has no element of symmetry is called what?

Sol.

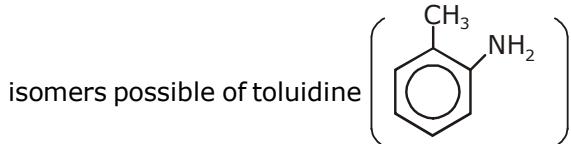
20. Draw all the possible stereoisomers of 3-pentene-2-ol.

Sol.

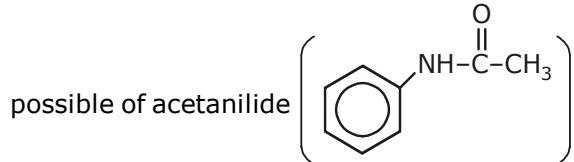
21. Draw optically active stereo isomer of the following compound.

**Sol.**

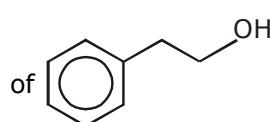
22. Calculate the number of aromatic 1°-amine

**Sol.**

23. Calculate the number of aromatic isomeric amides

**Sol.**

24. Calculate the number of isomeric ethers possible

**Sol.**

25. How many pair(s) of geometrical isomers are possible with C_5H_{10} (only in open chain structures)

Sol.

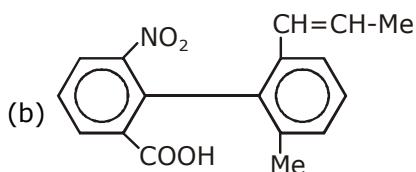
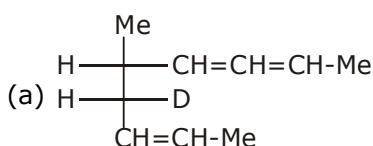
26. Total number of compounds with molecular formula C_5H_{10} which can show geometrical isomerism are (only cyclic)?

Sol.

27. How many enantiomers are possible on monochlorination of isopentane.

Sol.

31. Total stereoisomers of a given compound are ?



28. Find out the total number of cyclic isomers of C_5H_{10} which are optically active?

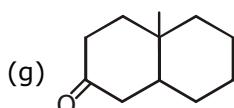
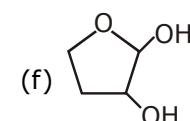
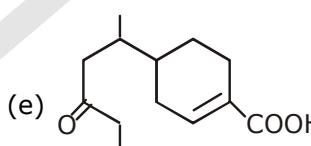
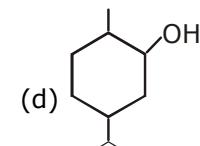
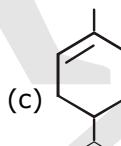
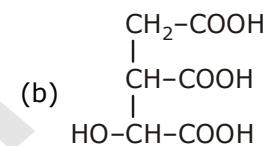
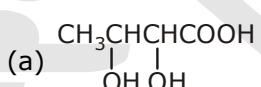
Sol.

Sol.

29. Calculate the total number of open chain isomeric compounds of molecular formula C_4H_8O which can show geometrical isomerism.

Sol.

32. Mark each chiral center in the following molecules with an asterisk. How many stereoisomers are possible for each molecule?



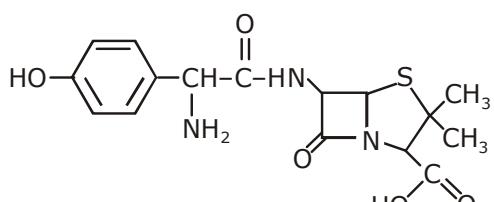
Sol.

30. How many stereoisomers exist for

- (a) 3-methylcyclopentanol?
- (b) 1,3-Cyclohexanediol?

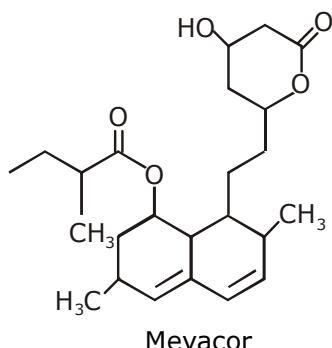
Sol.

33. (a) Label the four chiral centers in amoxicillin, which belongs to the family of semisynthetic penicillins.



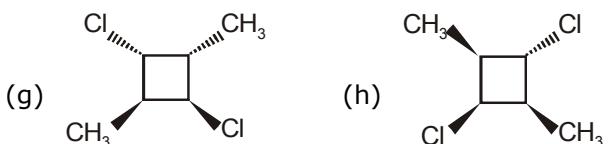
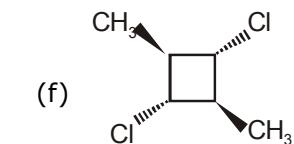
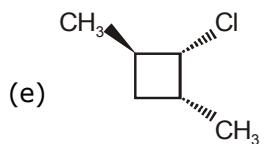
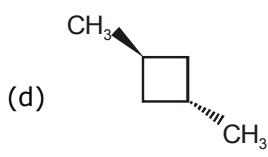
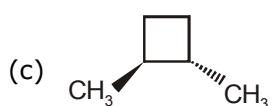
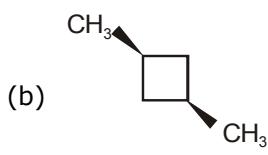
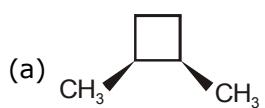
Amoxicillin

(b) Mevacor is used clinically to lower serum cholesterol levels. How many chirality centers does Mevacor have?



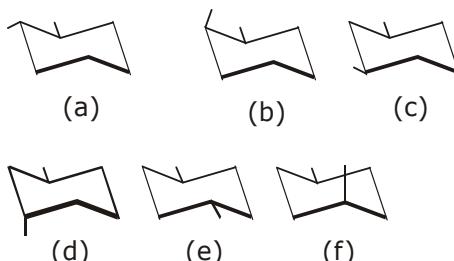
Sol.

34. Among the following How many compounds are chiral ?



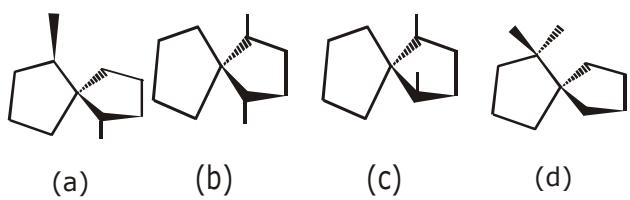
Sol.

35. Are the following structures chiral as drawn ? When placed in a solution at 298 K, which structure will show an optical rotation? Explain.



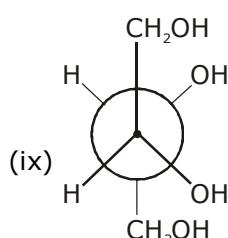
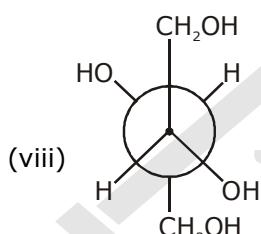
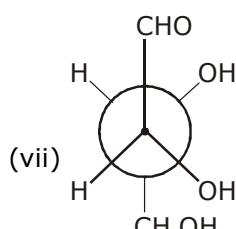
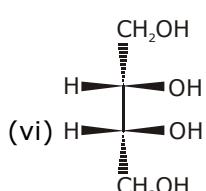
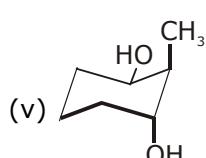
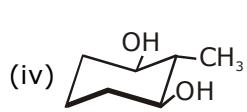
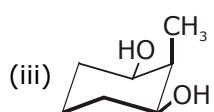
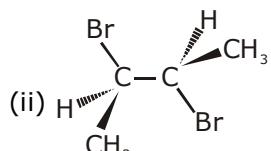
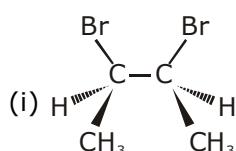
Sol.

36. Which of the following compounds are chiral ? Which, if any, are meso ?



Sol.

37. Among of the following how many are meso compounds ?



Sol.

38. Among the following compounds how many has a stereoisomer that is a meso compound ?

(a) (i) 2,3-dimethylbutane
 (ii) 2-bromo-3-methylpentane
 (iii) 1-bromo-2-methylcyclohexane

(b) (i) 3,4-dimethylhexane
 (ii) 3,4-diethylhexane
 (c) (i) 1,3-dimethylcyclohexane
 (ii) 1,4-dimethylcyclohexane
 (iii) 1,2-dimethylcyclohexane

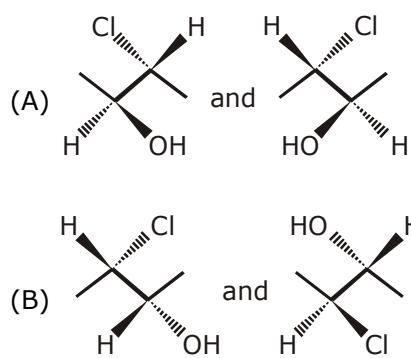
Sol.

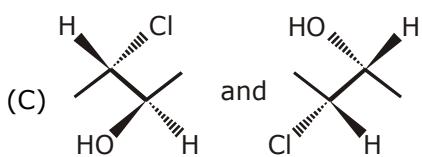
39. How many compounds among the following have a stereoisomer that is achiral ?

(a) (i) 2,3-dichlorobutane
 (ii) 2,3-dichloropentane
 (iii) 2,3-dichloro-2,3-dimethylbutane
 (b) (i) 1,2-dimethylcyclobutane
 (ii) 1,3-dibromocyclobutane
 (iii) 1,3-dichlorocyclopentane
 (iv) 1,2-dimethylcyclopentane
 (c) (i) 2,4-dibromopentane
 (ii) 2,3-dibromopentane
 (iii) 1,4-dimethylcyclohexane

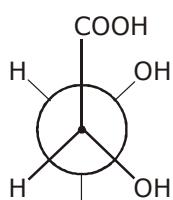
Sol.

40. Are the formulas within each set identical, enantiomers, or diastereomers ?

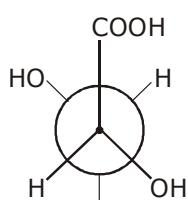


**Sol.**

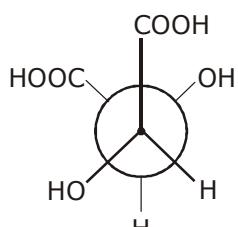
41. Following are four Newman projection formulas for tartaric acid.



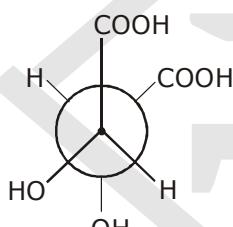
(1)



(2)



(3)

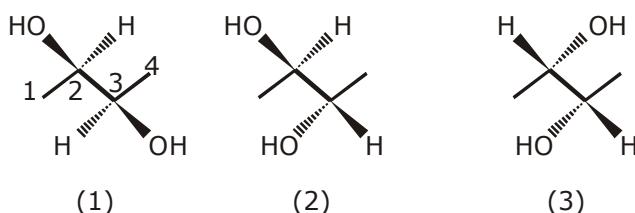


(4)

(a) Which represent the same compound ?
 (b) Which represent enantiomers ?
 (c) Which represent a meso compound ?
 (d) Which are diastereomers ?

Sol.

42. Following are stereorepresentations for the three stereoisomers of 2,3-butanediol. The carbons are numbered beginning from the left, as shown in (1).

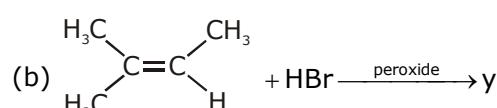
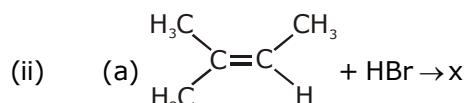


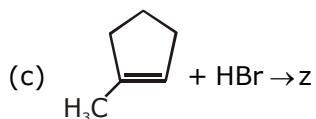
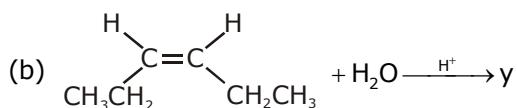
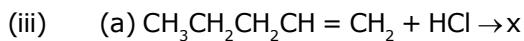
(a) Assign an R or S configuration to each chiral center.
 (b) Which are enantiomers ?
 (c) Which is the meso compound ?
 (d) Which are diastereomers ?

Sol.

43. Find out the total number of major products (including stereoisomers) are obtained in each of the following reactions.

(i) (a) 1-butene + HCl \rightarrow x
 (ii) 1-butene + HBr + peroxide \rightarrow y
 Find the value of (x + y) ?



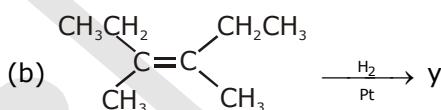
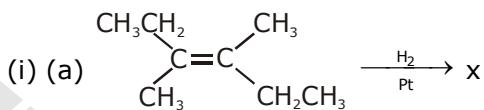


Find the value of $(x + y + z)$?

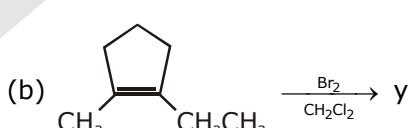
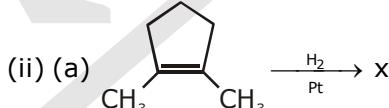
Sol.

Sol.

45. Find out the total number of major products (including stereoisomers) are obtained in each of the following reactions.



Find the value of $(x + y + z)$?



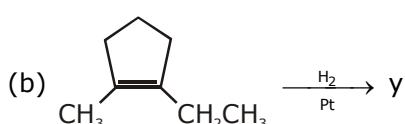
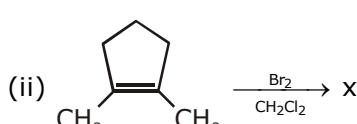
find the value of $(x+y)$?

Sol.

44. Find out the total number of major products (including stereoisomers) are obtained in each of the following reactions.



Find the value of $(x + y + z)$?



EXERCISE – IV**LEVEL – I****PREVIOUS YEARS****JEE MAIN**

Q.1 Stereo - Isomerism includes -
[AIEEE-2002]
 (A) Geometrical isomerism only
 (B) Optical isomerism only
 (C) Both geometrical & optical isomerism
 (D) Position & Functional isomerism

Sol.

Q.4 Geometrical isomerism is not shown by -
[AIEEE-2002]

(A) 1, 1- dichloro-1-pentene
 (B) 1, 2- dichloro-1-pentene
 (C) 1, 3- dichloro-2-pentene
 (D) 1, 4- dichloro-2-pentene

Sol.

Q.2 Which of the following does not show geometrical isomerism -
[AIEEE-2002]
 (A) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
 (B) $\text{CH}_3 - \text{CH}_2 - \text{HC} = \text{CH}_2$
 (C) $\text{CH}_3 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_3$
 (D) $\text{ClHC} = \text{CH} - \text{CH}_2 - \text{CH}_3$

Sol.

Q.5 Racemic mixture is - **[AIEEE-2002]**
 (A) A mixture of chiral carbons
 (B) A mixture of isomers
 (C) A mixture of aldehydes and ketones
 (D) A mixture of alcohols and ethers

Sol.

Q.3 Racemic mixture is formed by mixing two -
[AIEEE-2002]
 (A) Isomeric compounds
 (B) Chiral compounds
 (C) Meso compounds
 (D) Enantiomers with chiral carbon

Sol.

Q.6 Among the following four structures I to IV

(i) $\text{C}_2\text{H}_5-\overset{\text{CH}_3}{\text{CH}}-\text{C}_3\text{H}_7$ (ii) $\text{C}_2\text{H}_5-\overset{\text{O}}{\text{C}}-\overset{\text{CH}_3}{\text{CH}}-\text{C}_2\text{H}_5$
 (iii) $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}^{\oplus}$ (iv) $\text{C}_2\text{H}_5-\overset{\text{CH}_3}{\text{CH}}-\text{C}_2\text{H}_5$

It is true that - **[AIEEE-2003]**

(A) Only (iii) is a chiral compound
 (B) Only (ii) and (iv) are chiral compounds
 (C) All four are chiral compounds
 (D) Only (i) and (ii) are chiral compounds

Sol.

Q.7 Which of the following compounds is not chiral? **[AIEEE-2004]**

- 1 - chloropentane
- 2 - chloropentane
- 1 - chloro - 2 - methyl pentane
- 3 - chloro - 2 - methyl pentane

Sol.

Q.8 Which of the following will have a mesoisomer also - **[AIEEE-2004]**

- 2 - Chlorobutane
- 2, 3 - Dichlorobutane
- 2,3 - Dichloropentane
- 2-Hydroxypropanoic acid

Sol.

Q.9 Which types of isomerism is shown by 2,3-dichlorobutane? **[AIEEE-2005]**

- Optical
- Diastereo
- Structural
- Geometric

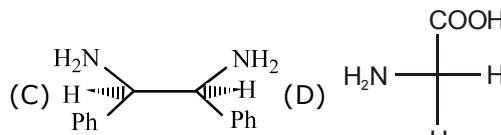
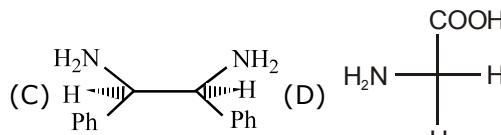
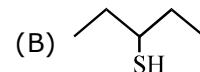
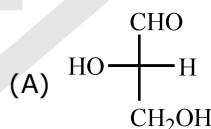
Sol.

Q.10 Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is **[AIEEE 2006]**

- Gauche, Eclipse, Anti
- Eclipse, Anti, Gauche
- Anti, Gauche, Eclipse
- Eclipse, Gauche, Anti

Sol.

Q.11 Which of the following molecules is expected to rotate the plane of plane-polarised light? **[AIEEE-2007]**

**Sol.**

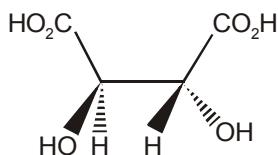
Q.12 Which one of the following conformations of cyclohexane is chiral?

[AIEEE-2007]

(A) Twist boat	(B) Rigid
(C) Chair	(D) Boat

Sol.

Q.13 The absolute configuration of



[AIEEE-2008]

(A) R, R	(B) R, S
(C) S, R	(D) S, S

Sol.

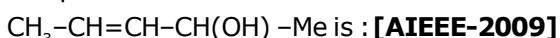
Q.14 The alkene that exhibits geometrical isomerism is:

[AIEEE-2009]

(A) propene	
(B) 2-methyl propene	
(C) 2-butene	
(D) 2- methyl -2- butene	

Sol.

Q.15 The number of stereoisomers possible for a compound of the molecular formula



(A) 3	(B) 2
(C) 4	(D) 6

Sol.

Q.16 Out of the following, the alkene that exhibits optical isomerism is

[AIEEE-2010]

(A) 3-methyl-2-pentene	
(B) 4-methyl-1-pentene	
(C) 3-methyl-1-pentene	
(D) 2-methyl-2-pentene	

Sol.

Q.17 How many chiral compounds are possible on monochlorination of 2-methyl butane?

(A) 4	(B) 6
(C) 8	(D) 2

Sol.

LEVEL - II**JEE ADVANCED**

1. The number of isomers for the compound with molecular formula $C_2BrClFI$ is [JEE 2001(Scr.)]

(A) 3 (B) 4 (C) 5 (D) 6

Sol.

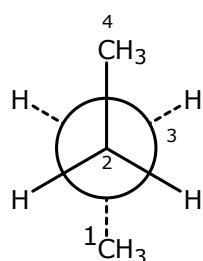
2. Which of the following compounds exhibits stereoisomerism ? [JEE 2002(Scr.)]

(A) 2-methylbutene-1 (B) 3-methylbutyne-1
 (C) 3-methylbutanoic acid (D) 2-methylbutanoic acid

Sol.

3. In the given conformation, if C_2 is rotated about $C_2 - C_3$ bond anticlockwise by an angle of 120° then the conformational obtained is

[JEE 2004(Scr.)]



(A) fully eclipsed conformation
 (B) partially eclipsed conformation
 (C) gauche conformation
 (D) staggered conformation

Sol.

$$\text{4. (i)} \mu_{\text{obs}} = \sum_i \mu_i x_i$$

where μ_i is the dipole moment of a stable conformer of the molecule, $Z - CH_2 - CH_2 - Z$ and x_i is the mole fraction of the stable conformer.

Given : $\mu_{\text{obs}} = 1.0 \text{ D}$ and x (Anti) = 0.82

Draw all the stable conformers of $Z - CH_2 - CH_2 - Z$ and calculate the value of $\mu_{(\text{Gauche})}$.

(ii) Draw the stable conformer of $Y - CHD - CHD - Y$ (meso form), when $Y = CH_3$ (rotation about $C_2 - C_3$) and $Y = OH$ (rotation about $C_1 - C_2$) in Newmann projection. [JEE 2005]

Sol.

5. The number of structural isomers for C_6H_{14} is

[JEE 2007]

(A) 3 (B) 4 (C) 5 (D) 6

Sol.

6. Statement-1: Molecules that are not superimposable on their mirror images are chiral, because

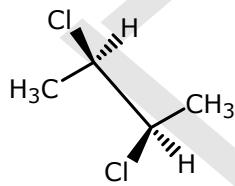
Statement-2: All chiral molecules have chiral centres.
[JEE 2007]

- (A) **Statement-1** is true, **statement-2** is true and **statement-2** is correct explanation for **statement-1**
- (B) **Statement-1** is true, **statement-2** is true and **statement-2** is NOT correct explanation for **statement-1**
- (C) **Statement-1** is true, **statement-2** is false
- (D) **Statement-1** is false, **statement-2** is true

Sol.

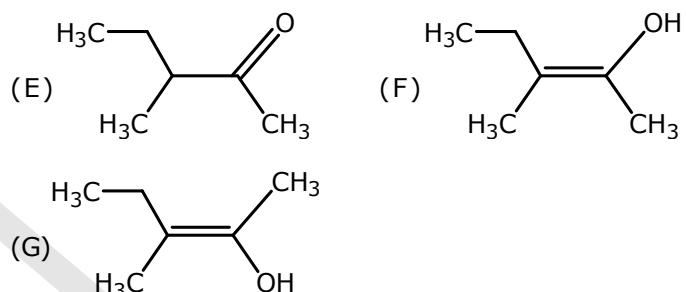
Sol.

7. The correct statement(s) about the compound given below is (are)
[JEE 2008]



- (A) The compound is optically active
- (B) The compound possesses centre of symmetry
- (C) The compound possesses plane of symmetry
- (D) The compound possesses axis of symmetry

8. The correct statement(s) concerning the structures E, F and G is (are)
[JEE 2008]



- (A) E, F and G resonance structures
- (B) E, F and E, G are tautomers
- (C) F and G are geometrical isomers
- (D) F and G are diastereomers

Sol.

9. The correct statement(s) about the compound $\text{H}_3\text{C}(\text{OH})\text{HC} - \text{CH} = \text{CH} - \text{CH}(\text{OH})\text{CH}_3(\text{X})$ is (are)
[JEE 2009]

- (A) The total number of stereoisomers possible for X is 6
- (B) The total number of diastereomers possible for X is 3
- (C) If the stereochemistry about the double bond in X is trans, the number of enantiomers possible for X is 4.
- (D) If the stereochemistry about the double bond in X is cis, the number of enantiomers possible for X is 2.

Sol.

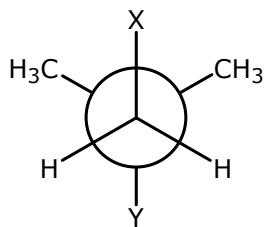
10. The total number of cyclic structural as well as stereo isomers possible for compound with the molecular formula C_5H_{10} is [JEE 2009]

Sol.

11. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is

Sol.

Sol. **12.** In the Newman projection for 2, 2-dimethylbutane [JEE 2010]

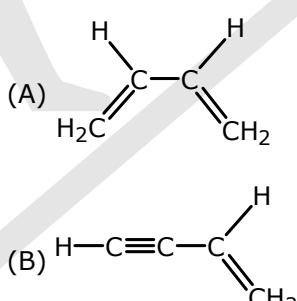


X and Y can respectively be

Sol.

13. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (in any), is (are)

[JEE 2011]



(C) $\text{H}_2\text{C} = \text{C} = \text{O}$
(D) $\text{H}_2\text{C} = \text{C} = \text{CH}_2$

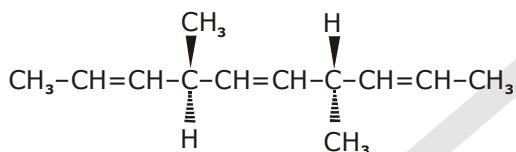
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14. In Allene (C_3H_4), the type (s) of hybridisation of the carbon atoms is (are) [JEE 2012]

(A) sp and sp^3 (B) sp and sp^2
 (C) only sp^2 (D) sp^2 and sp^3

Sol.

15. The number of optically active product obtained from the complete ozonolysis of the given compound is [JEE 2012]



(A) 0

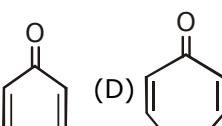
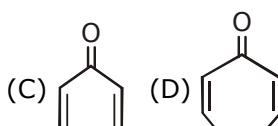
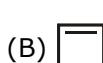
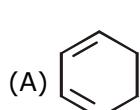
Sol.

(B) 1

(C) 2

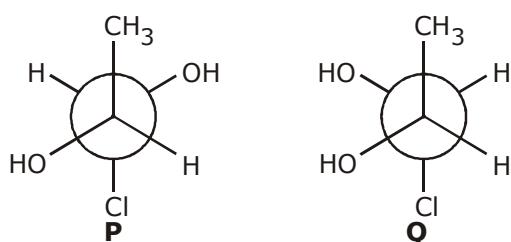
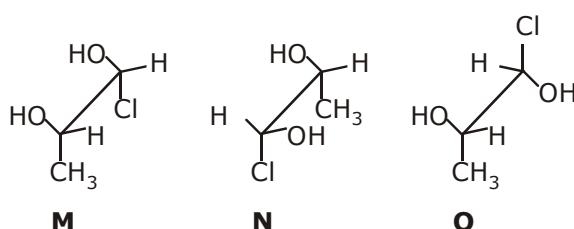
(D) 4

16. Which of the following molecules in pure form is (are) unstable at room temperature [JEE 2012]



Sol.

17. Which of the given statement(s) about N, O, P and Q with respect to M is (are) correct? [JEE 2012]



(A) M and N are non-mirror image stereoisomers
 (B) M and O are identical
 (C) M and P are enantiomers
 (D) M and Q are identical

Sol.

Answers

Answer Ex-I
JEE MAIN

1. C	2. A	3. B	4. A	5. C	6. A	7. B
8. C	9. C	10. A	11. C	12. D	13. A	14. D
15. B	16. A	17. D	18. D	19. D	20. B	21. A
22. C	23. C	24. C	25. D	26. A	27. C	28. C
29. C	30. D					

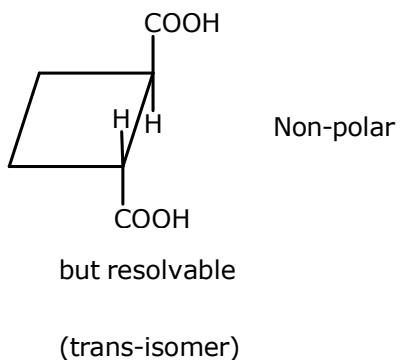
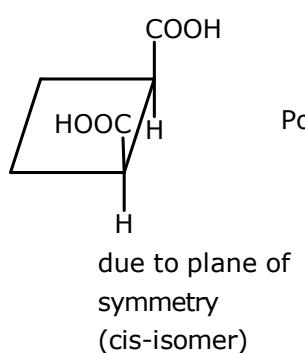
Answer Ex-II
JEE ADVANCED (OBJECTIVE)

1. B	2. B	3. B	4. B	5. D	6. B	7. D
8. A	9. C	10. C	11. C	12. D	13. C	14. D
15. B	16. A	17. B	18. D	19. C	20. C	21. D
22. D	23. C	24. C	25. A	26. C	27. C	28. B
29. B	30. A	31. D	32. C	33. B	34. C	35. D
36. C	37. C	38. A	39. B	40. A	41. C	42. A
43. A	44. C	45. C	46. B	47. C	48. B	49. B
50. D	51. C	52. D	53. B	54. C	55. B	56. B

57. A	58. B	59. A	60. AD	61. ABC	62. D	63. BC
64. ABC	65. BCD	66. AC	67. AD	68. B	69. C	70. C
71. ABC	72. ACD	73. ACD	74. ACD	75. ACD	76. AC	77. BC
78. ABCD		79. (A) Q, S; (B) Q, S; (C) P, S; (D) Q, R		80. (A) P, R; (B) S; (C) P, R; (D) P, Q, S		
81. (A) R, (B) P, (C) S, (D) S			82. (A) P, Q, R (B) Q, R, S (C) Q, R, S (D) P, Q, R			
83. A → P; B → R; C → Q; D → R			84. B	85. B	86. D	

Answer Ex-III**JEE ADVANCED**

1. c
2. (I) Diasteromers (ii) Enantiomers (iii) Identical
3. (I) Identical (ii) Diastereomers (iii) Diastereomers
4. (a) E (b) D (c) I
5. (a) E (b) I (c) D (d) I (e) E
6. (a) Diastereomers (b) diastereomers (c) not isomer (d) structural (e) Enantiomer
7. (a) Dia (b) Not isomer (c) Enenatiomers (d) Structural isomers (e) Identical
8. (i) achiral, (ii) achiral, (iii) Chiral, (vi) Chiral, (v) achiral
9. Compound I is optically inactive since it contain a plane of symmetry. Compound II is enantiomeric since it does not contain plane of symmetry. Hence chiral. Also compound I is polar while II non polar.
10. (A) Column (a) Chiral (b) chiral (c) meso (d) chiral
 (B) Column (a) enantiomers (b) enantiomers (c) diastereomers (d) diastereomers
11. The compound must be 1, 2-cyclobutan-dicarboxylic acid since all other constitutional isomerers are non-resolvable.



12. 3

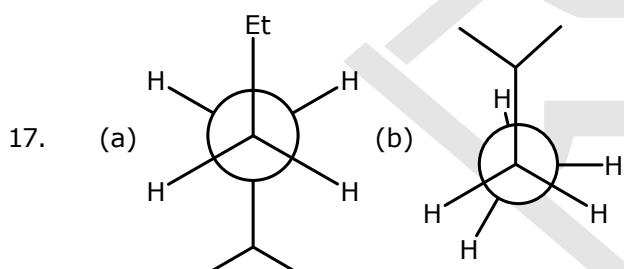
13. (i) Et -O - Et, (ii) $\text{CH}_3 - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ (iii) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$, (iv) $\text{CH}_3 - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$

I and II metamers, I & III functional isomers, III & IV position isomers.

14. (I) 4, (II) 3, (III) 4

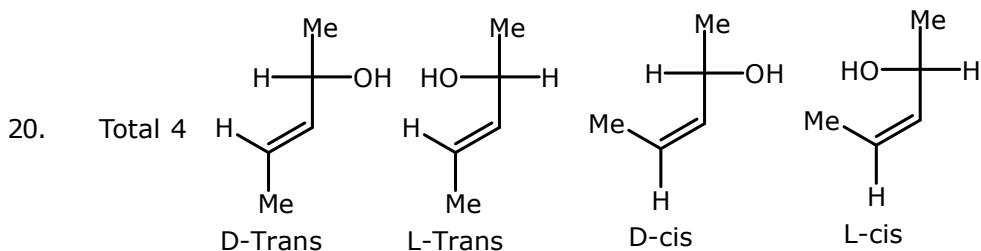
15. Optical : a, b, c, d, f, g, i, k; Geometrical isomer : c, g, j ; None : e, h,

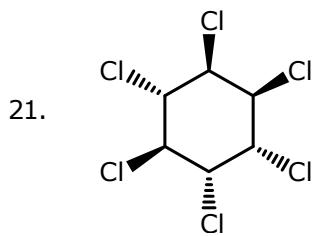
16. achiral : I, III; chiral : II, IV, V, VI



18. (a) cis (b) cis (c) cis (d) trans (e) trans (f) trans

19. D



**22. 4****23. 9****24. 5****25. 1****26. 1****27. 2****28. 2****29. 2****30. (a) 4 (b) 3****31. (a) 16 (b) 4****32. (a) 4 (b) 4 (c) 2 (d) 8 (e) 4 (f) 4 (g) 4****33. (a) 4 (b) 8****34. 3****35. 2****36. chiral → a, b ; meso → c****37. 5****38. (a) 0 (b) 1 (c) 2****39. (a) 2 (b) 4 (c) 2****40. (a) enantiomer (b) enantiomer (c) diastereomers****41. (a) 3 & 4 (b) 1 & 3, 1 & 4 (c) 2****(d) 1 & 2, 2 & 3, 2 & 4****42. (a) 2R 3R, 2R 3S, 2S 3S (b) 1 & 3****(c) 2 (d) 1 & 2 ; 2 & 3****43. (i) 3 (ii) 3 (iii) 5****44. (i) 5 (ii) 4****45. (i) 5 (ii) 3****Answer Ex-IV****PREVIOUS YEARS****LEVEL - I****JEE MAIN****1. C****2. B****3. D****4. A****5. A****6. D****7. A****8. B****9. A****10. B****11. A****12. A****13. A****14. C****15. C****16. C****17. A****LEVEL - II****JEE ADVANCED****1. D****2. D****3. C****4. (i) $\frac{1}{0.18}$ D (ii) Anti form when Y = CH₃ & Gauche when Y = -OH****5. C****6. C****7. AD****8. BCD****9. AD****10. 7****11. 5****12. BD****13. BC****14. B****15. A****16. BC****17. ABC**

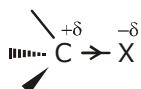
ALKYL HALIDE

1.1 ALIPHATIC HALOGEN DERIVATIVES:

Compounds obtained by the replacement of one or more hydrogen atom(s) from hydrocarbons are known as halogen derivatives. The halogen derivatives of alkanes, alkenes, alkynes and arenes are known as alkyl halide (haloalkene), alkenyl halide (haloalkenes), alkynyl halides (haloalkynes) and aryl halides (halobenzenes) respectively.

Alkyl halides : Monohalogen derivatives of alkanes are known as alkyl halides

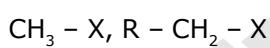
Structure of alkyl halides:



Classification of alkyl halides :

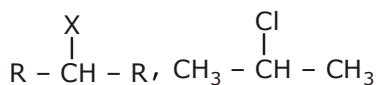
(i) Primary halide : If the halogen bearing carbon is bonded to one carbon atom or with no carbon atom

Example :



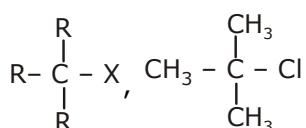
(ii) Secondary halide : If two carbon atoms are bonded to the halogen bearing carbon.

Example :



(iii) Tertiary halide : Three other carbon atom bonded to the halogen bearing carbon atom.

Example :



Halokanes can be classified into following three categories.

(i) Monohaloalkanes (ii) Dihaloalkanes (iii) Polyhaloalkanes

1.2 IUPAC NOMENCLATURE OF ALKYL HALIDES

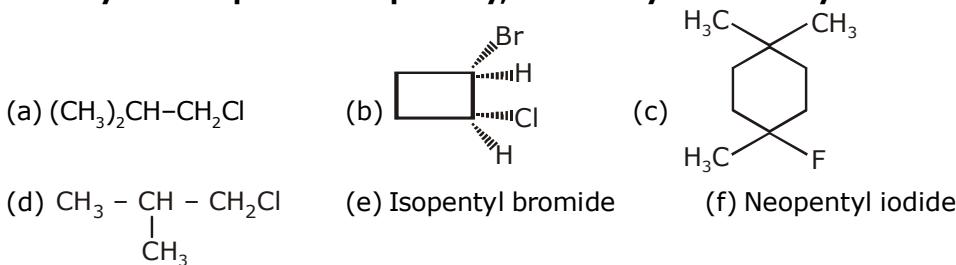
S.N.	Compound	IUPAC name
1.		2 - Chloro-2-methylpropane
2.		3-Bromo-1-chlorobutane
3.		2-Bromo-1-chloro-4-fluoro-3-methylbutane
4.		2-Bromo-1-chloro-3-iodocyclopentane
5.		5-chloropentan-2-ol
6.		5-Fluoropent-1-ene
7.		Chlorophenylmethane
8.		Dichlorophenylmethane
9.		Trichlorophenylmethane
10.		2,2-Bis(chloromethyl)-1,3-dichloropropane
11.		Cis-1,4-dibromocyclohexane
12.		2-iodo-3-phenylbutane

1.4 BONDING IN ALKYL HALIDE:

Table : 1 Carbon halogen bond lengths

Bond	Bond length(Å)
CH ₃ – F	1.39
CH ₃ – Cl	1.78
CH ₃ – Br	1.93
CH ₃ – I	2.14

Ex.1 Classify the compound as a primary, secondary and tertiary halide



Sol. (a) Primary (b) Secondary (c) Tertiary (d) Primary
 (e) Primary (f) Primary

1.5 PHYSICAL PROPERTIES OF ALKYL HALIDE:

1.5.1 Dipole moment of the halogen derivatives:

$$\mu = 4.8 \times \delta \times d$$

Where δ is the charge and d is the bond length

These two effects e.g. charge and distance oppose each other, with the larger halogens having longer bond but weaker electronegativity. The overall result is that the bond dipole moment increase in the order.

$$\begin{array}{ll} \text{C} - \text{I} < \text{C} - \text{Br} < \text{C} - \text{F} < \text{C} - \text{Cl} \\ \mu : 1.29 \text{ D} \quad 1.48 \text{ D} \quad 1.51 \text{ D} \quad 1.56 \text{ D} \end{array}$$

The electronegativities of the halogen increase in the order:

$$\text{I} < \text{Br} < \text{Cl} < \text{F}$$

Table : 2 Molecular dipole moments of methylhalides

X	CH ₃ X	CH ₂ X ₂	CHX ₃	CX ₄
F	1.82 D	1.97 D	1.65 D	0
Cl	1.94 D	1.60 D	1.03 D	0
Br	1.79 D	1.45 D	1.02 D	0
I	1.64 D	1.11 D	1.00 D	0

1.5.2 Boiling point :

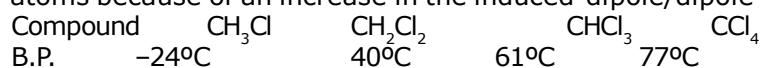
(a) With respect to the halogen in a group of alkyl halides, the boiling point increases as one descends the periodic table. Alkyl fluorides have the lowest boiling points and alkyl iodides have the highest boiling point. This trend matches the order of increasing polarizability of the halogens. (Polarizability is the ease with which the electrons distribution around an atom is distorted by a nearby electric field and is a significant factor in determining the strength of induced-dipole/induced-dipole and dipole/induced-dipole attractions.) Forces that depend on induced dipoles are strongest when the halogen is a highly polarizable iodine, and weakest when the halogen is a nonpolarizable fluorine.

Table : 3 Boiling points of some alkyl halide in °C (1 atm)

Formula	X = F	X = Cl	X = Br	X = I
CH ₃ - X	- 78	- 24	3	42
CH ₃ - CH ₂ X	- 32	12	38	72
CH ₃ - CH ₂ - CH ₂ X	- 3	47	71	103
CH ₃ - (CH ₂) ₃ - CH ₂ X	65	108	129	157
CH ₃ - (CH ₂) ₄ - CH ₂ X	92	134	155	180

Fluorine is unique among the halogens is that increasing the number of fluorines does not lead to higher and higher boiling point.

(b) The boiling points of the chlorinated derivatives of methane increase with the number of chlorine atoms because of an increase in the induced-dipole/dipole attractive forces.

**Table : 4**

	CH ₃ - CH ₂ F	CH ₃ - CHF ₂	CH ₃ - CF ₃	CF ₃ - CF ₃
B.P.	-32°C	- 25°C	- 47°C	- 78°C

1.5.3 Density :

Alkyl fluorides and chlorides are less dense and alkyl bromides and iodides more dense, than water.

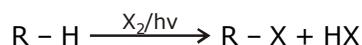
Table : 5

	CH ₃ - (CH ₂) ₆ - CH ₂ F	CH ₃ - (CH ₂) ₆ - CH ₂ Cl	CH ₃ - (CH ₂) ₆ - CH ₂ Br	CH ₃ - (CH ₂) ₆ - CH ₂ I
Density (20°C)	0.80 g/mL	0.89 g/mL	1.12 g/mL	1.34 g/mL

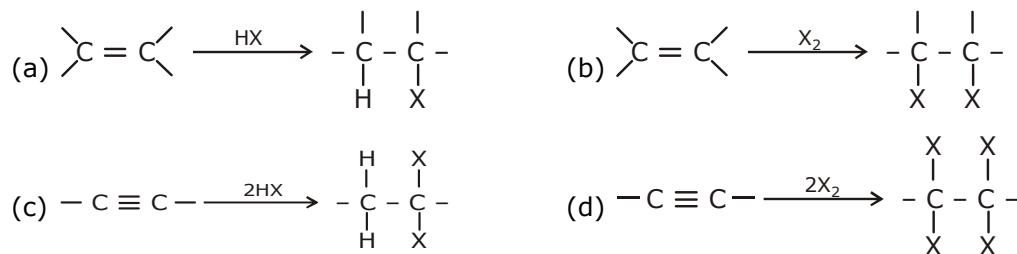
Because alkyl halides are insoluble in water, mixture of an alkyl halide and water separates into two layers. When the alkyl halides in a fluoride or chloride, it is on the upper layer and water is the lower. The situation is reversed when the alkyl halide is a bromide or an iodide. In these cases the alkyl halide is in the lower layer. Polyhalogenation increases the density. The compounds CH₂Cl₂, CHCl₃ and CCl₄, for example, are all more dense than water.

1.6 PREPARATION OF ALKYL HALIDE :

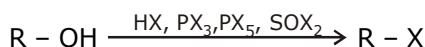
1.6.1 From alkane :



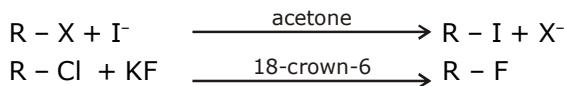
1.6.2 From alkenes and alkynes (Detail in alkene and alkyne)



1.6.3 From alcohol (Detail in the alcohol)



1.6.4 From other halides



Finkelstein Reaction

1. $\text{CH}_3 - \text{CH}_2 - \text{Cl} \xrightarrow{\text{NaI/acetone}} \text{CH}_3 - \text{CH}_2 - \text{I}$
 Nucleophilicity – in Polar Protic solvent – $\text{F}^\ominus < \text{Cl}^\ominus < \text{Br}^\ominus < \text{I}^\ominus$
 Polar Aprotic solvent – $\text{F}^\ominus > \text{Cl}^\ominus > \text{Br}^\ominus > \text{I}^\ominus$
 Covalent Nature : $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$
 Solubility in polar solvent ↓



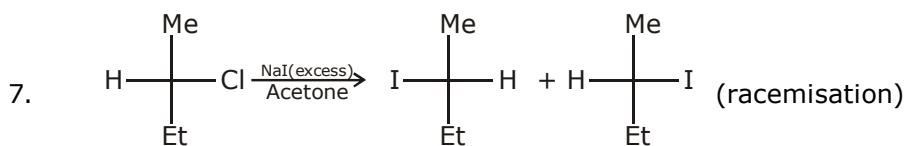
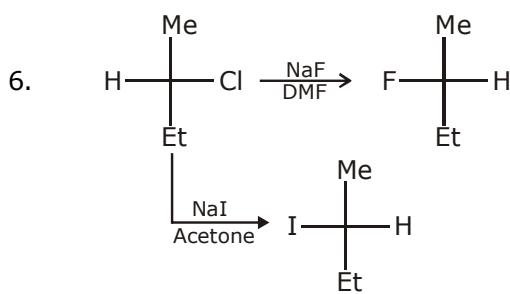
Acetone → Solubility in acetone is soluble
 $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$

2. $\text{C} - \text{C} - \text{Br} \xrightarrow[\text{Acetone}]{\text{NaBr}} \text{C} - \text{C} - \text{Br}$

3. $\text{C} - \text{C} - \text{Cl} \xrightarrow[\text{Acetone}]{\text{NaCl}} \text{C} - \text{C} - \text{Cl}$

4. $\text{C} - \text{C} - \text{Cl} \xrightarrow[\text{Acetone}]{\text{NaF}} \text{C} - \text{C} - \text{F}$

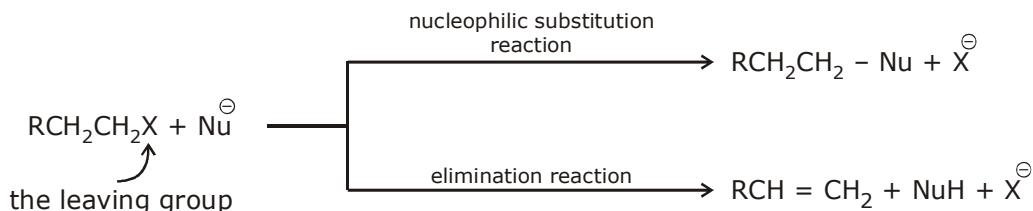
5. $\text{C} - \text{C} - \text{Cl} \xrightarrow[\text{or DMSO}]{\text{KF/DMF}} \text{C} - \text{C} - \text{F}$ (swart reaction)



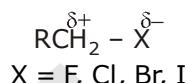
1.7 CHEMICAL REACTIONS OF ALKYL HALIDE:

1.6.4 Nucleophilic substitution reaction:

Those organic compounds in which an sp^3 hybridized carbon is bonded to an electronegative atom or group can undergo two type of reaction e.g. substitution reactions in which the electronegative atom or group is replaced by another atom or group. Second is elimination reaction in which the electronegative atom or group is eliminated along with hydrogen from an adjacent carbon. The electronegative atom or group which is substituted or eliminated is known as leaving group.



Because of more electronegativity of halogen atom it has partial negative charge and partial positive charge develops on carbon atom.



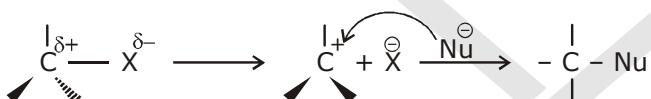
Due to this polar carbon - halogen bond alkyl halides shows nucleophilic substitution and elimination reaction.

There are two important mechanisms for the substitution reaction

(1) A nucleophile is attracted to the partially positively charged carbon. As the nucleophile approaches the carbon, it causes the carbon - halogen bond to break heterolytically (the halogen keeps both of the bonding electrons.)

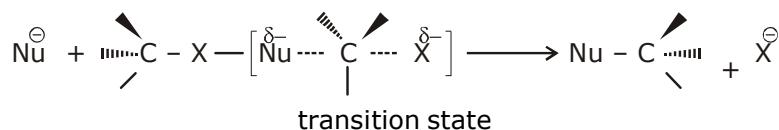


(2) The carbon-halogen bond breaks heterolytically without any assistance from the nucleophile, by the help of polar protic solvent and carbocation is formed (solvolytic). Formed carbocation then reacts with the nucleophile to form the substitution product.



(A) Bimolecular nucleophilic substitution reaction (S_N^2)

The mechanism of S_N^2 reaction



Characteristic of S_N^2

(1) It is bimolecular, unistep process

(2) It is second order reaction because in the Rds two species are involved

(3) Kinetics of the reaction → rate \propto [alkyl halide] [nucleophile]
rate \propto k[alkyl halide] [nucleophile]

If the concentration of alkyl halide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is double. If the concentration of nucleophile is doubled the rate of reaction is also double. If the concentration of both are doubled then the rate of the reaction quadruples.

(4) Energetics of the reaction →

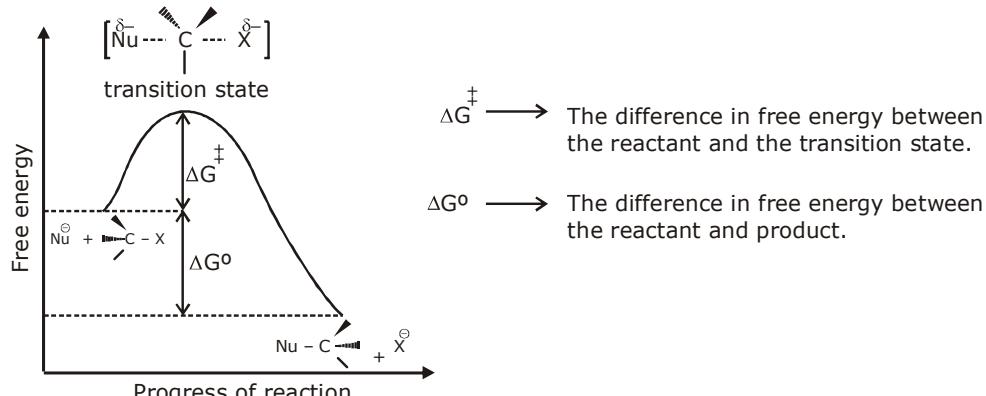
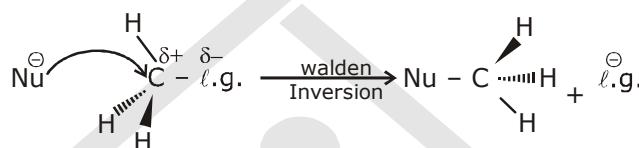


Figure : A free energy diagrams for a hypothetical S_N^2 reaction that takes place with a negative ΔG°

(5) No intermediates are formed in the S_N^2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.

(6) The stereochemistry of S_N^2 reaction → As we seen earlier, in an S_N^2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes a inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as walden inversion.



(7) Factor's affecting the rate of S_N^2 reaction → Number of factors affect the relative rate of S_N^2 reaction, the most important factors are

- Structure of the substrate
- Concentration and reactivity of the nucleophile
- Effect of the solvent
- Nature of the leaving group

(i) Effect of the structure of the substrate →

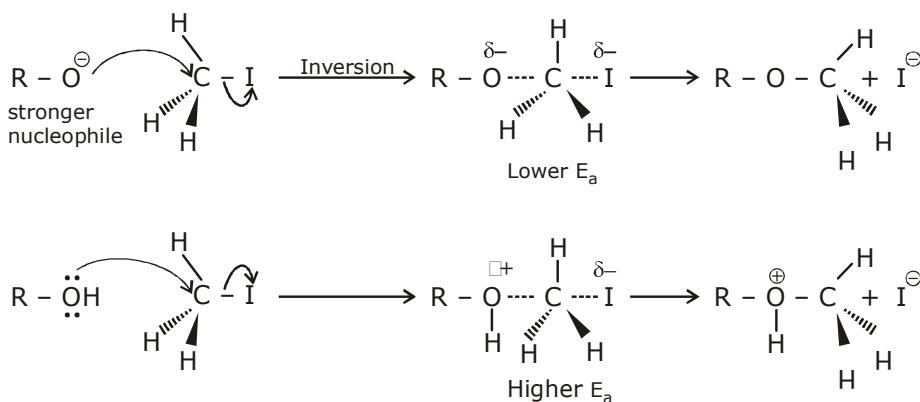
Order of reactivity in S_N^2 reaction : $-CH_3 > 1^\circ > 2^\circ >> 3^\circ$ (unreactive)

the important factor behind this order of reactivity is a steric effect. Very large and bulky groups can often hinder the formation of the required transition state and crowding raises the energy of the transition state and slows down reaction.

Table : 6 Relative rates of reactions of alkyl halide in S_N^2 reaction.

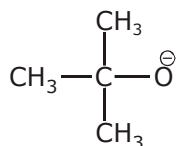
Substituent	Compound	Relative rate
Methyl	CH_3X	30
1°	CH_3CH_2X	1
2°	$(CH_3)_2CHX$	0.02
Neopentyl	$(CH_3)_3CCH_2X$	0.00001
3°	$(CH_3)_3CX$	~0

(ii) According to kinetics of S_N^2 increasing the concentration of the nucleophile increases the rate of an S_N^2 reaction. The nature of nucleophile strongly affect the rate of S_N^2 reaction. A stronger nucleophile is much more effective than a weaker. For example we know that a negatively charged nucleophile is more reactive than its conjugate acid e.g. $HO^- > H_2O$, $RO^- > ROH$.

**Table : 7**

some common nucleophiles listed in decreasing order of nucleophilicity in hydroxylic solvent	
Strong nucleophiles ($\text{CH}_3\text{CH}_2)_3\ddot{\text{P}}$	Moderate nucleophile : Br^-
$-\ddot{\text{S}}\text{H}$	$\text{NH}_3^{\cdot\cdot}$
I^-	$(\text{CH}_3)_2\ddot{\text{S}}^-$
$(\text{CH}_3-\text{CH}_2)_2\ddot{\text{N}}\text{H}$	Cl^-
$-\text{CN}^-$	ACO^-
$(\text{CH}_3-\text{CH}_2)_3\ddot{\text{N}}^-$	Weak nucleophile F^-
HO^-	H_2O
CH_3O^-	CH_3OH

Steric effects on nucleophilicity

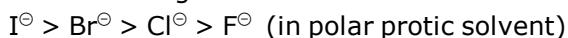


t-butoxide
Stronger base, yet weaker nucleophile cannot approach the carbon atom so easily.



ethoxide weaker base, yet stronger nucleophile

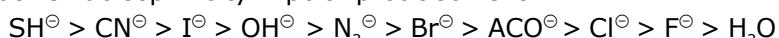
(iii) The effect of the solvent → In polar protic solvent large nucleophiles are good, and the halide ions show the following order



This effect is related to the strength of the interaction between nucleophile and solvent molecules of polar protic solvent forms hydrogen bond to nucleophiles in the following manner.

Because small nucleophile is solvated more by the polar protic solvent thus its nucleophilicity decreases and rate of S_{N}^2 decreases

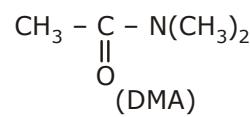
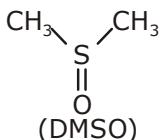
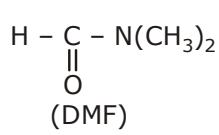
Relative nucleophilicity in polar protic solvent



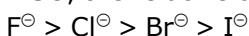
So, polar protic solvents are not useful for rate of S_{N}^2 , if nucleophile is anionic. But polar aprotic

solvent does not have any active hydrogen atom so they can not form H bond with nucleophiles. Polar aprotic solvent have crowded positive centre, so they do not solvate the anion appreciably therefore the rate of S_N^2 reactions increased when they are carried out in polar aprotic solvent.

Examples of polar aprotic solvent.

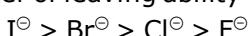


In DMSO, the relative order of reactivity of halide ions is

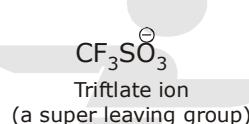
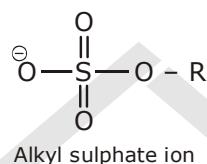
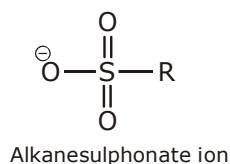


(iv) The nature of the leaving group → The best leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving group are good, which stabilise negative charge most effectively and weak base do this best, so weaker bases are good leaving groups. A good leaving group always stabilize the transition state and lowers its free energy of activation and thereby increases the rate of the reaction.

Order of leaving ability of halide ion



Other leaving groups are



Strongly basic ions rarely act as leaving group →

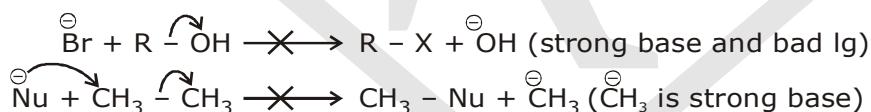
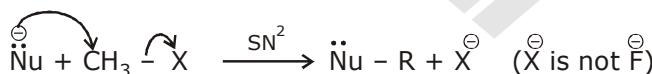


Table : 8 Examples of S_N^2 reactions of alkyl halide →



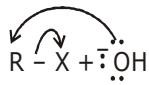
Nucleophile

Product

Class of Product



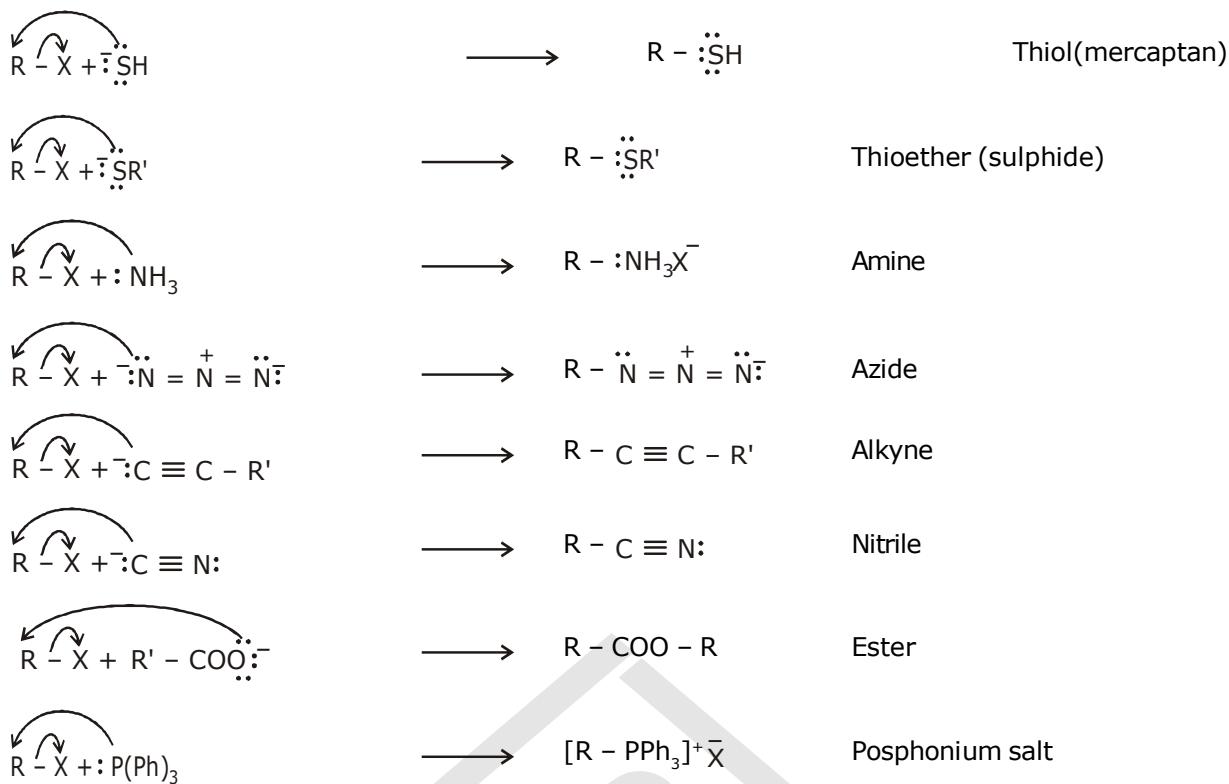
Alkyl halide



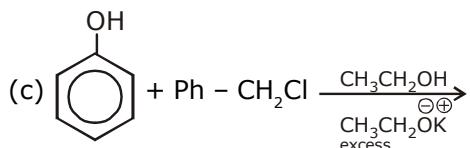
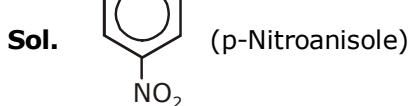
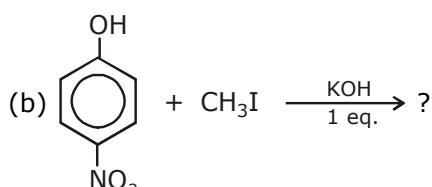
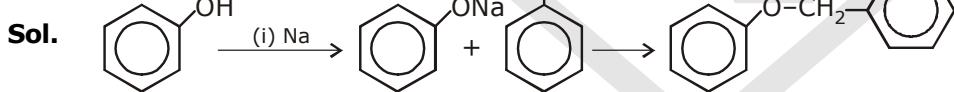
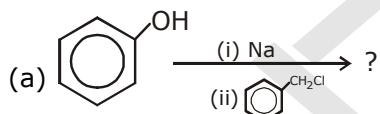
Alcohol



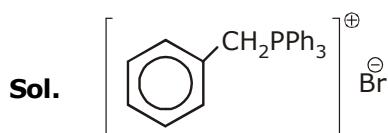
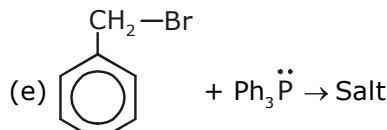
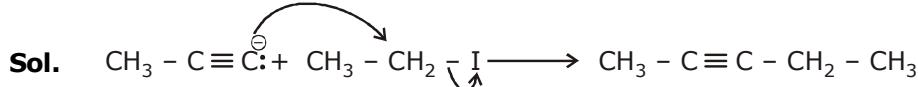
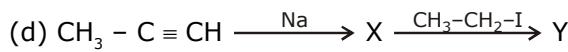
Ether



Ex. Complete the following reactions with mechanism



Sol. $\text{CH}_3\text{-CH}_2\text{-O}^\ominus$ is present in excess and it is stronger nucleophile than Ph-O^\ominus so product is $\text{Ph-CH}_2\text{-OEt}$



Ex. When the concentration of alkyl halide is tripled and the concentration of OH^- ion is reduced to half, the rate of S_N^2 reaction increases by :

(A) 3 times (B) 2 times (C) 1.5 times (D) 6 times

Ans. C

Ex. In the given reaction, $\text{CH}_3\text{CH}_2\text{-X} + \text{CH}_3\text{SNa} \rightarrow$
The fastest reaction occurs when 'X' is –

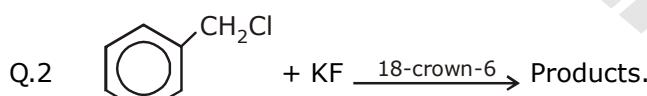
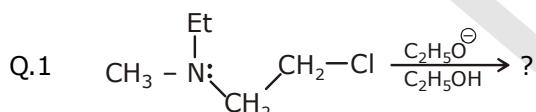
(A) $-\text{OH}$ (B) $-\text{F}$ (C) $-\text{OCOCF}_3$ (D) $-\text{OCOCH}_3$

Ans. C

Ex. Correct decreasing order of reactivity towards S_N^2 reaction

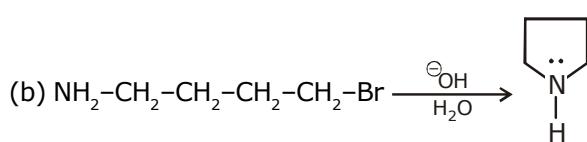
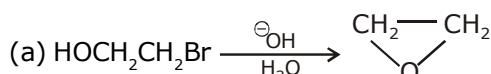
(I) $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{Et}}{ \text{N}}} \text{CHCH}_2\text{Cl}$	(II) $\text{CH}_3\overset{\text{CH}_3}{\underset{\text{Et}}{ \text{N}}} \text{CHCH}_2\text{CH}_2\text{Cl}$	(III) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	(IV) $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{CH}_3}{\underset{\text{Et}}{ \text{N}}} \text{CHCl}$
(A) IV > I > II > III	(B) III > II > I > IV	(C) IV > I > III > II	(D) II > I > IV > III

Ans. B

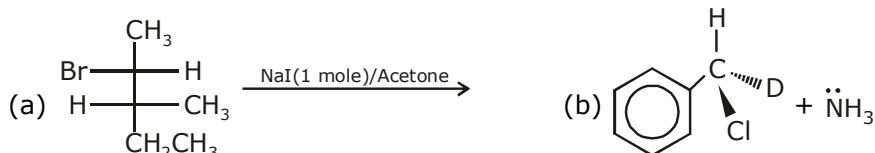


What is the function of 8 corwn-6?

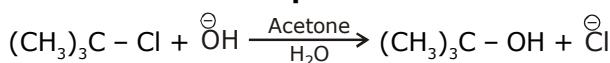
Q.3 Write mechanisms that account for the product of the following reactions:



Q.4 Draw a Fischer projection for the product of the following S_N^2 reaction

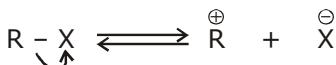


(B) Unimolecular nucleophilic substitution reaction (S_N^1):

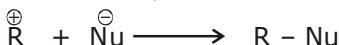


Mechanism of S_N^1 reaction :

Step - 1 Formation of a carbocation (Rate determining step)



Step - 2 Nucleophilic attack on the carbocation (fast)



Characteristics of S_N^1 reactions

1. It is unimolecular, two step process and intermediate is formed, (intermediate is carbocation)

2. It is first order reaction

3. Kinetics of the reaction

$$\text{Rate} \propto [\text{Alkyl halide}]$$

$$\text{Rate} = k[(\text{CH}_3)_3\text{C}-\text{X}]$$

Rate of S_N^1 reaction is independent of concentration and reactivity of nucleophile.

4. Energetics of the S_N^1

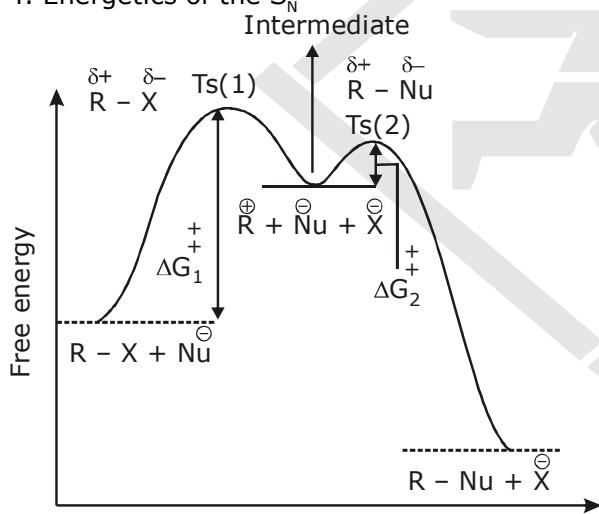


Figure : free energy diagram for the S_N^1 reaction.

5 Factor's affecting the rates of S_N^1

5.(i) The structure of the substrate →

The Rds of the S_N^1 reaction is ionization step, in this step form a carbocation. This ionisation is strongly endothermic process, rate of S_N^1 reaction depends strongly on carbocation stability because carbocation is the intermediate of S_N^1 reaction which determines the energy of activation of the reaction.

S_N^1 reactivity : $3^\circ > 2^\circ > 1^\circ > \text{CH}_3-\text{X}$

5.(ii) Concentration and reactivity of the nucleophile →

The rate of S_N^1 reactions are unaffected by the concentration and nature of the nucleophile

5.(iii) Effect of the solvent → the ionizing ability of the solvent:

Because to solvate cations and anions so effectively the use of polar protic solvent will greatly

increase the rate of ionization of an alkyl halide in any S_N^1 reaction. It does this because solvation stabilizes the transition state leading to the intermediate carbocation and halide ion more than it does the reactant, thus the energy of activation is lower.

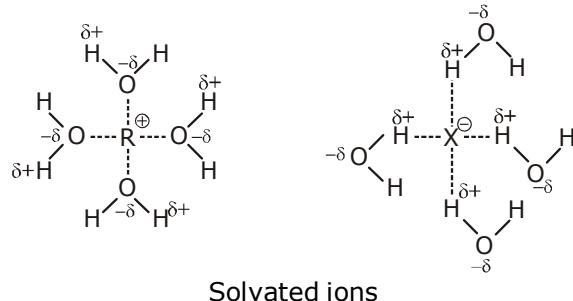
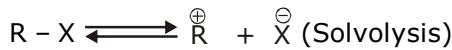


Table : 9 Dielectric constants (ϵ) and ionization rates of t-Butylchloride in common solvents

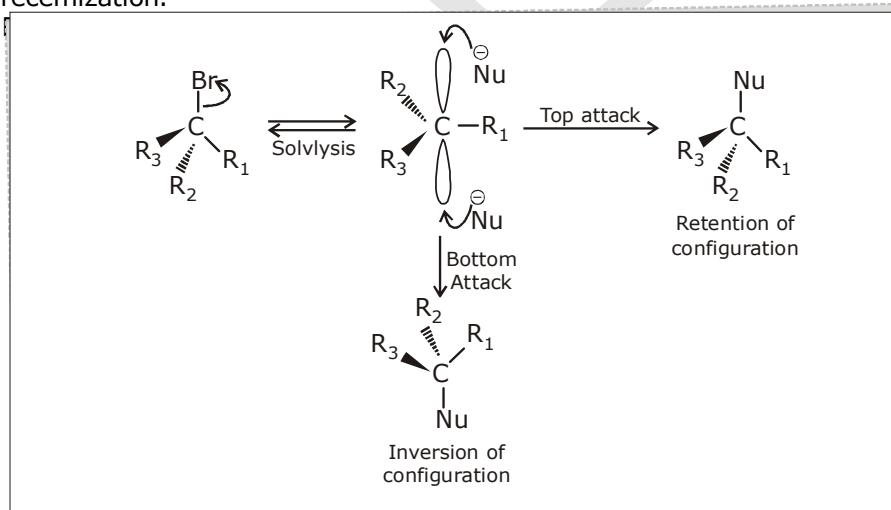
Solvent	ϵ	Relative rate
H_2O	80	8000
CH_3OH	33	1000
C_2H_5OH	24	200
$(CH_3)_2CO$	21	1
CH_3CO_2H	6	-

5.(iV) The nature of the leaving group \rightarrow

In the S_N^1 reaction the leaving group begins to acquire a negative charge as the transition state is reached. Stabilisation of this developing negative charge at the leaving group stabilizes the transition state and : this lowers the free energy of activation and thereby increases the rate of reaction.

leaving ability of halogen is $I^- > Br^- > Cl^- >> F^-$

6. Stereochemistry of S_N^1 reactions \rightarrow In the S_N^1 mechanism, the carbocation intermediate is sp^2 hybridized and planar. A nucleophile can attack on the carbocation from either face, if reactant is chiral then after attack of nucleophile from both faces gives both enantiomers of the product, which is called recemicization.



Comparison of S_N¹ and S_N² reactions :

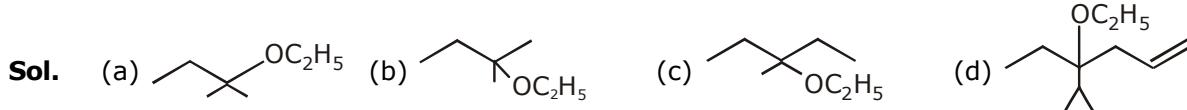
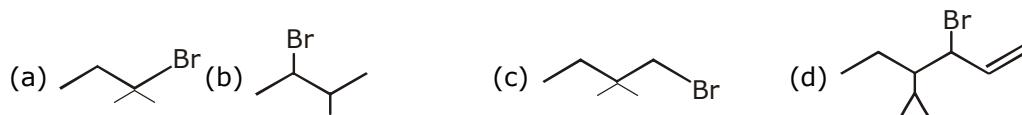
		S _N ¹	S _N ²
(i)	Effect of the nucleophile	Nucleophile strength is not important	Stronger nucleophile is required
(ii)	Effect of the substrate	$3^{\circ} > 2^{\circ} > 1^{\circ} > \text{CH}_3\text{X}$	$\text{CH}_3\text{X} > 1^{\circ} > 2^{\circ}$
(iii)	Effect of solvent	Good ionizing solvent required	It goes faster in less polar solvent, if Nu ⁻ is present
(iv)	Kinetics	Rate = k [R-X]	Rate = k[R-X] [Nu ⁻]
(v)	Stereochemistry	Racemisation	walden inversion
(vi)	Rearrangement	common	Impossible

Ex. 6 Predict the compound in each pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

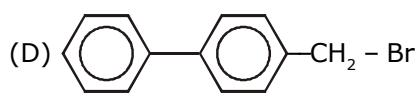
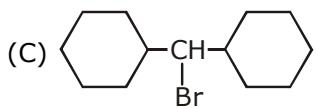
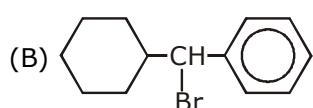
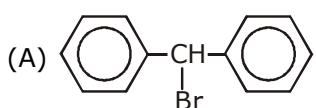
	I	II
(a)	$(\text{CH}_3\text{CH}_2)_2\text{CH}-\text{Cl}$	$(\text{CH}_3)_3\text{CCl}$
(b)		
(c)		
(d)		
(e)		

Sol. (a) II > I (b) II > I (c) I > II (d) II > I (e) II > I

Ex. 7 Give the solvolysis products expected when each compound is heated in ethanol

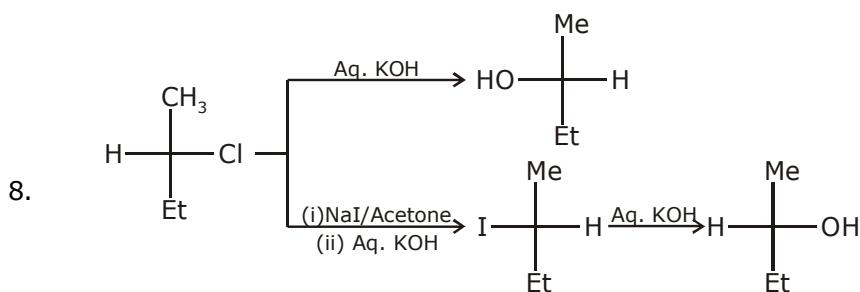
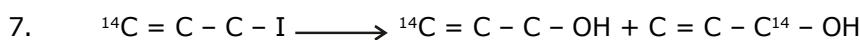
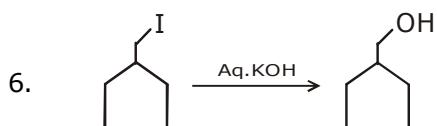
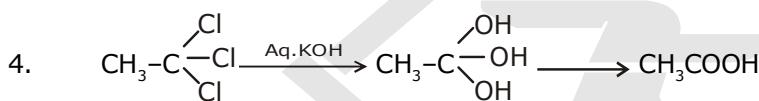
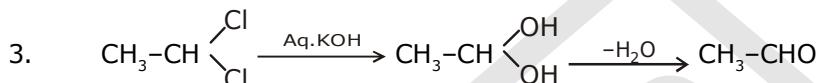
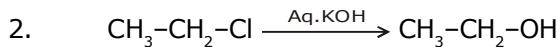
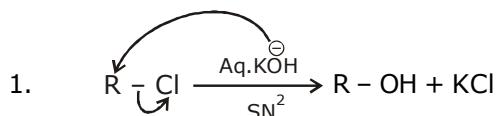


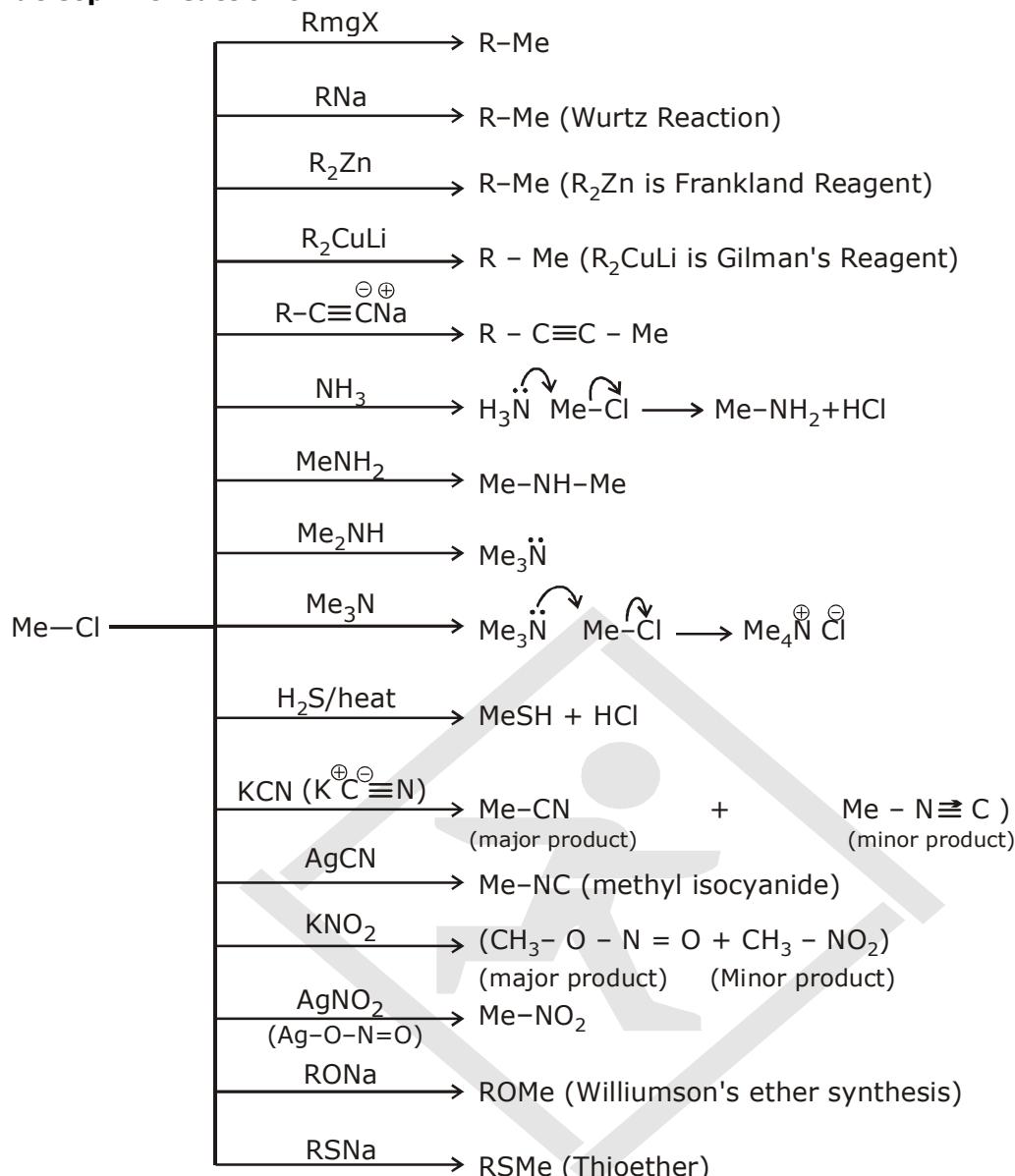
Ex.8 The rate of S_N^1 reaction is fastest with



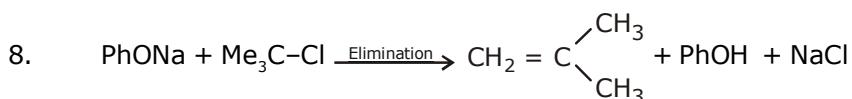
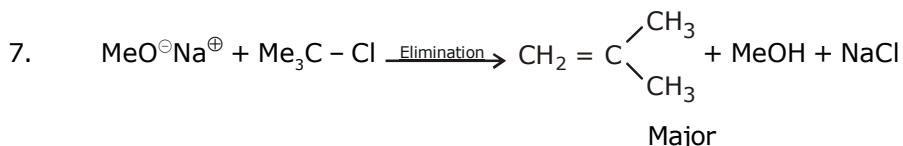
Ans. (A)

Reaction of RX with aq. KOH

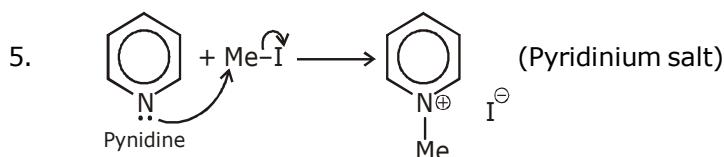
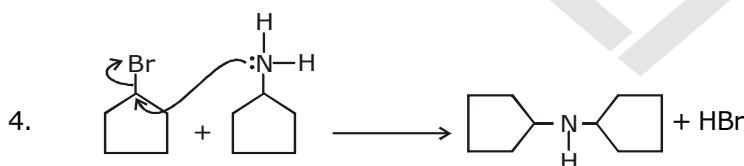
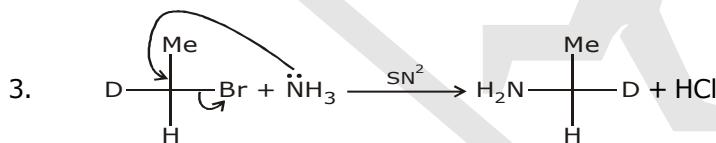
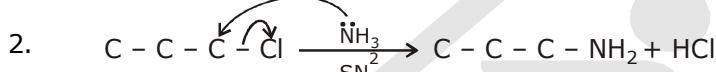
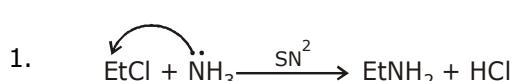


Other Nucleophilic reaction of R – X :-**WilliamSon's Ether Synthesis: (SN²)**

1. $\text{R}-\text{O}^{\oplus}\text{Na}^{\ominus} + \text{R}-\text{Cl} \longrightarrow \text{R}-\text{O}-\text{R} + \text{NaCl}$
2. EtONa + Me – Cl → EtOMe
3. MeONa + Et – Cl → EtOMe
Rate (2) > (3) 2 is better method. (Due to less steric hindrance)
4. MeONa + PhCl $\xrightarrow{\text{(lone pair is in resonance)}}$ No reaction

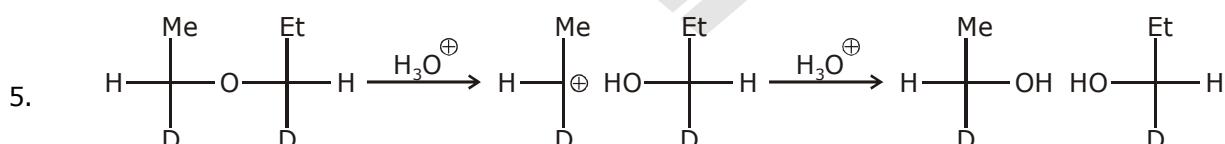
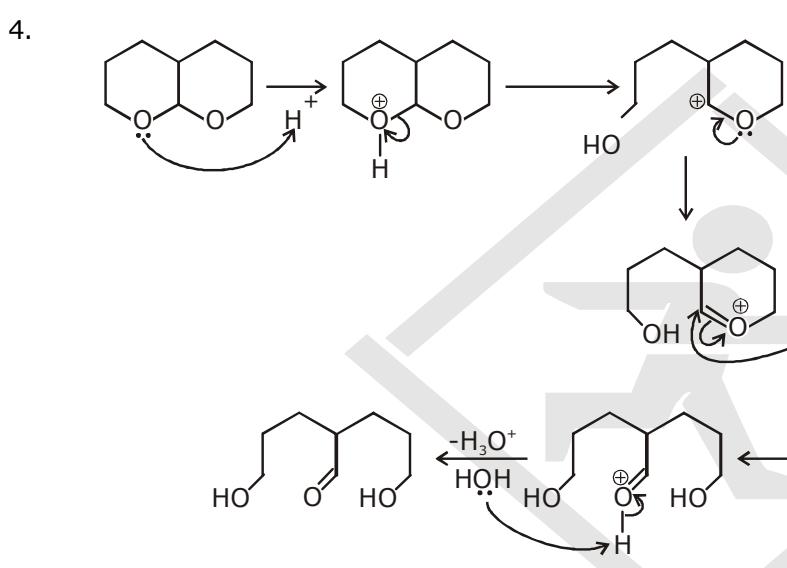
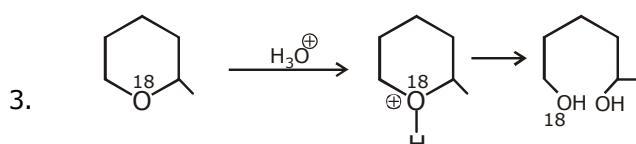
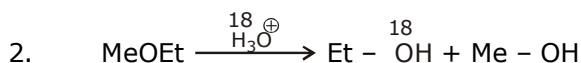
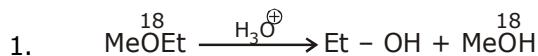


9. $\text{Me}_3\text{CONa} + \text{Ph-Cl} \longrightarrow \text{No. reaction}$
 $\text{Me}_3\text{CO-Ph}$ can not be prepared by Williamson's ether synthesis.

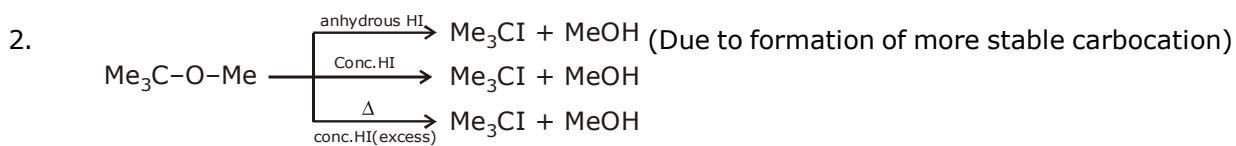
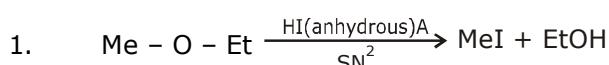


Some Other reactions

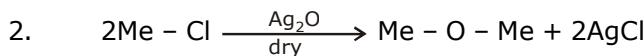
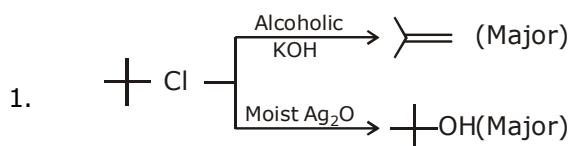
Hydrolysis of Ether



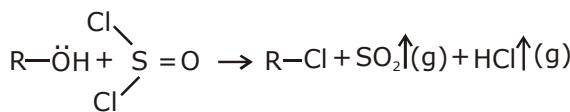
Reaction of ether with HI :



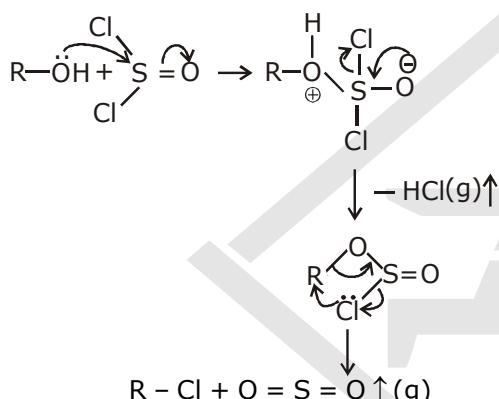
With moist and dry Ag_2O :



**SN_i (Nucleophilic substitution intramolecular)
(Darzon's process)**



Mech.



Note : (1) In SN_i retention of configuration takes place.

Note : (2) In presence of pyridine above reaction follow the SN^2 reaction mechanism.

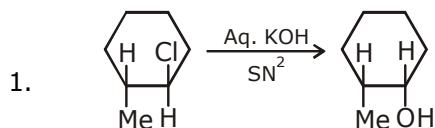
SN_{NGP} (Neighbouring group participation)

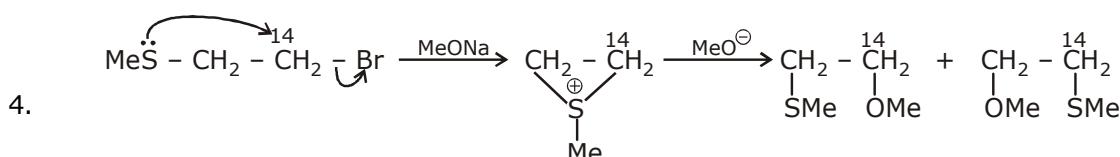
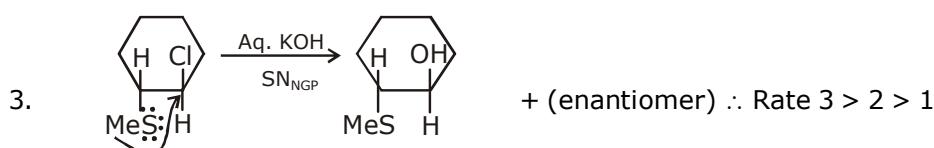
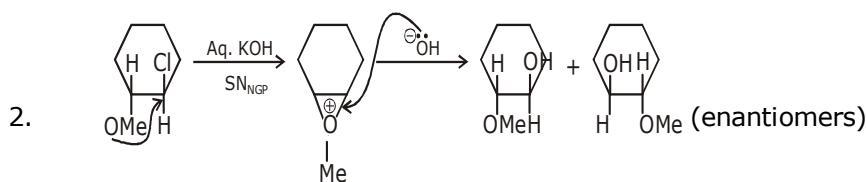
Increase in rate of SN reaction due to attack of internal nucleophile is called as SN_{NGP} is also known as Anchimeric assistance.

For SN_{NGP} :

1. Internal nucleophile must be present
2. Internal nucleophile must be anti to Ig.

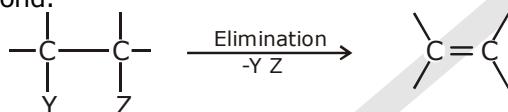
During NGP :-





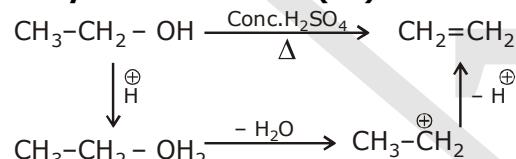
1.7.2 Elimination reactions:

In an elimination reaction two atoms or groups (YZ) are removed from the substrate with formation of pi bond.



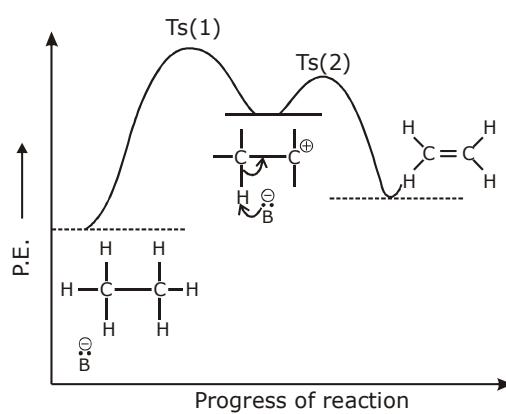
depending on the reagents and conditions involved, an elimination may be a first order (E_1) or second order (E_2).

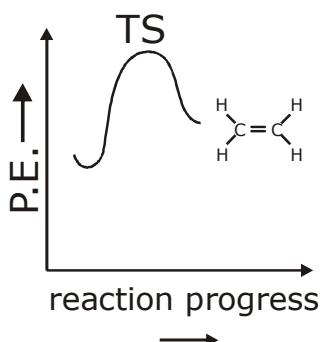
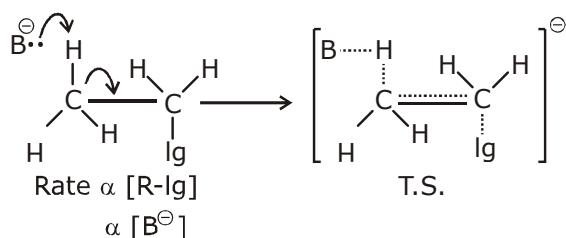
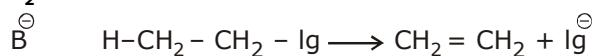
Dehydration of Alcohol (E_1)



Characteristics of E_1 reaction :

- (i) It is unimolecular, two step process
- (ii) It is first order reaction
- (iii) Reaction intermediate is carbocation, so rearrangement is possible
- (iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.
- (v) Kinetics \rightarrow Rate \propto [Substrate]
Rate = $k[\text{Substrate}]$



E₂- elimination :

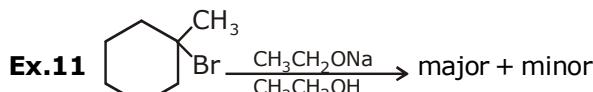
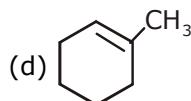
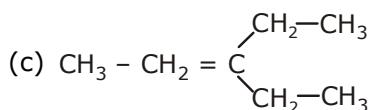
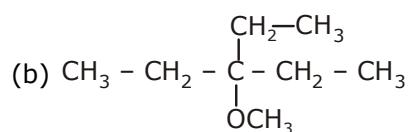
Bimolecular reaction, second order kinetic.

1. Leaving group leads when base is taking proton from adjacent carbon.
2. It is a single step reaction
3. Rate \propto single step reaction
Rate \propto Leaving group tendency
4. It shows elemental as well as kinetic isotopic effect with Ig as well as at β-position.
5. Normally saytzaff product is major.
6. Transition state mechanism therefore rearrangement is not possible.
7. The orientation of proton & leaving group should be antiperiplanar for E₂.
8. **Positional orientation of elimination** → In most E₁ and E₂ eliminations gives two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule (i.e., most stable alkene will be the major product)
9. E₂-elimination is favoured by :
 - (1) Moderate Ig
 - (2) Strong base (RO[⊖], Alc. KOH)
 - (3) Polar aprotic solvent.
 - (4) High conc. of base.
 - (5) High temperature

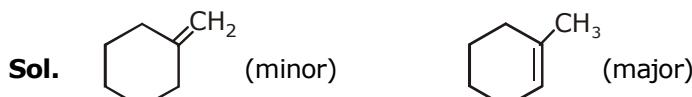
Ex. **Reactivity towards E₂** → R - I > R - Br > R - Cl > R - F
 Predict the elimination products of the following reactions.

(a) Sec. butyl bromide + NaOEt $\xrightarrow{\Delta}$ (b) 3-Bromo-3-ethylpentane + CH₃OH \longrightarrow
 (c) 2-Bromo-3-ethylpentane + MeONa $\xrightarrow{\Delta}$ (d) 1-Bromo-2-methylcyclohexane + EtONa $\xrightarrow{\Delta}$

Sol. (a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$



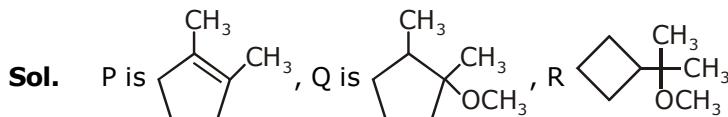
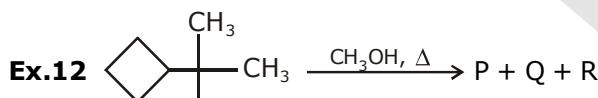
Write the structure of major and minor product.



Comparison of E₁ and E₂ elimination:

Promoting factors	E ₁	E ₂
(i) Base	Weak base	Strong base required
(ii) Solvent	Good ionizing solvent	Wide variety of solvent
(iii) Substrate	$3^\circ > 2^\circ > 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
(iv) Leaving group	Better one required	Better one required

Characteristics		
(i) Kinetics	$K[R-X]$, I st order	$K[R-X] [Base]$, II st order
(ii) Orientation	Saytzeff alkene	Saytzeff alkene
(iii) Stereochemistry	No special geometry is required	transition state must be co-planar



Q.6 Arrange the compounds of each set in order of reactivity towards dehydrohalogenation by strong base

(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(b) 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane-2-Bromo-3-methylbutane

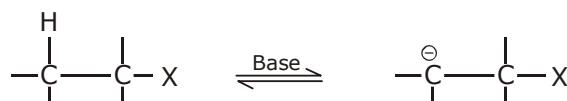
(c) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-Bromo-3-methylbutane

(C) mechanism of E₁ CB reaction (Unimolecular conjugate base reaction) :

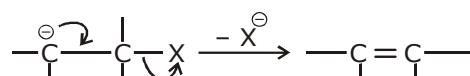
The E₁ CB or carbanion mechanism : In the E₁ CB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism:

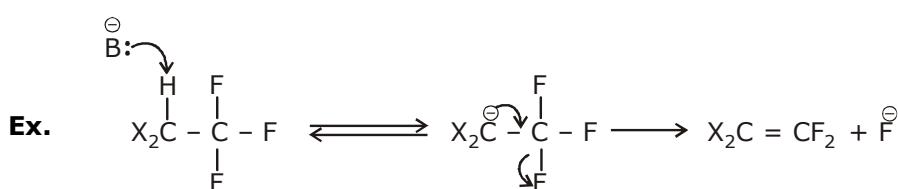
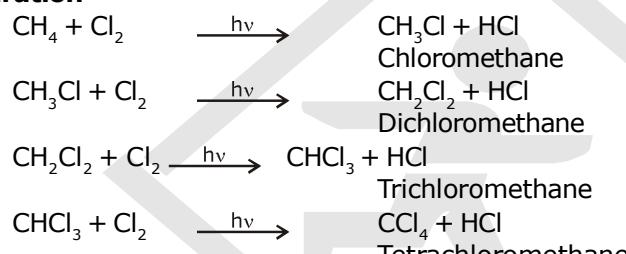
Step-1 : Consists of the removal of a proton, H^+ by a base generating a carbanion



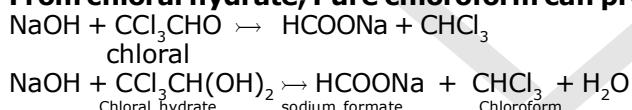
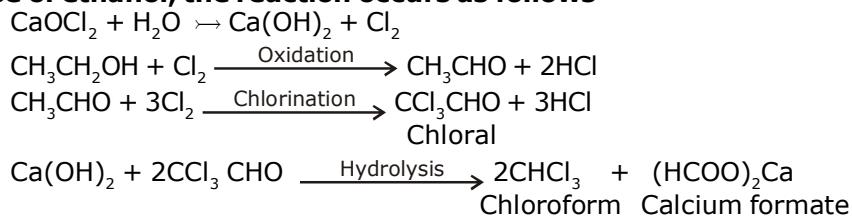
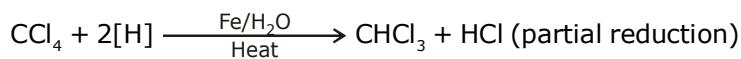
Step-2 : Carbanion loses a leaving group to form alkene

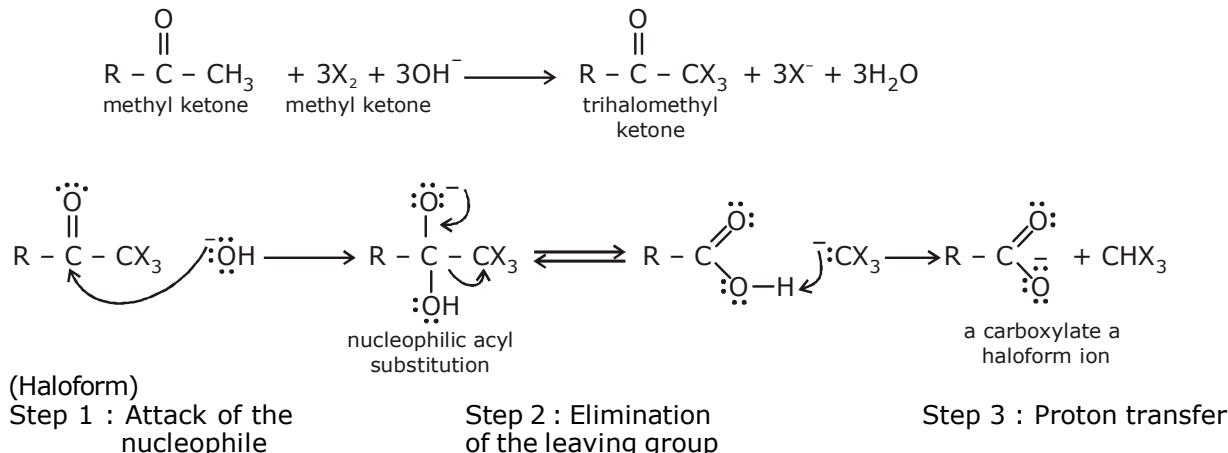


Condition: For the E_1 CB, substrate must be containing acidic hydrogens and poor leaving groups (i.e., bad ℓ/g)

**1.8 Polyhalogen derivatives****Trichloromethane (Chloroform), CHCl_3** **1.8.1 Preparation**

The mixture of CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 can be separated by fractional distillation.

2. From chloral hydrate, Pure chloroform can prepare.**3. Laboratory Method :** From ethanol or acetone by reaction with a paste of bleaching powder and water.**In case of ethanol, the reaction occurs as follows****4. From carbontetrachloride**

5. Haloform reaction

Prob. Compare rate of elimination (Dehydro halogenation in presence of alcoholic KOH) i.e., E2 :

1. (a) (b) (c) (d)

c > b > a > d

2. (a) (b) (c)

c > b > a

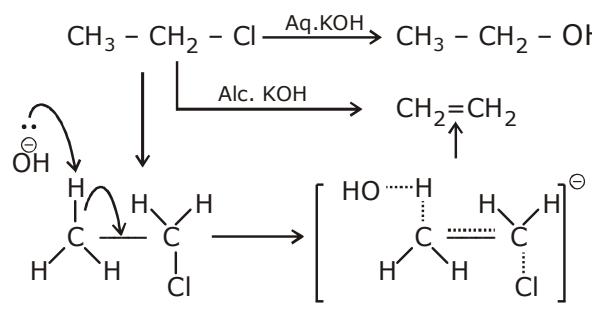
3. (a) (b) (c)

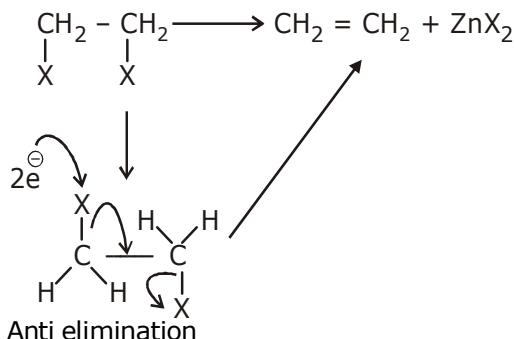
c > b > a

4. (a) (b) (c)

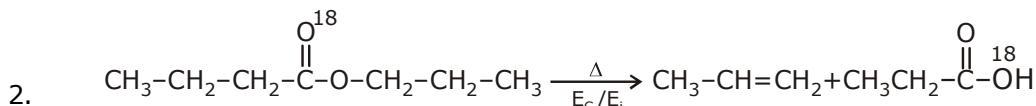
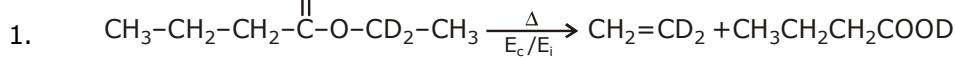
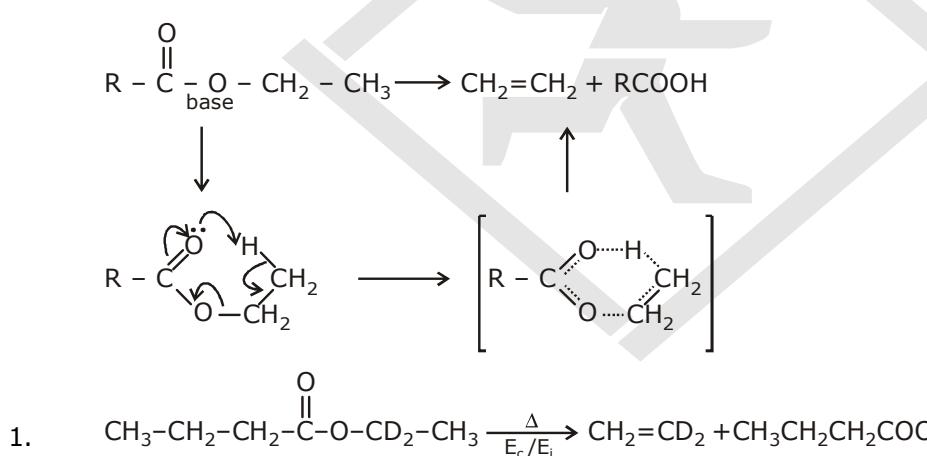
b > a > c

Dehydro halogenation (-HX) E2



Dehalogenation : - (-X₂) E2**E_c or E_i (Intramolecular or cyclic elimination mechanism):**

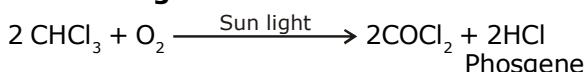
- (1) Lg and Base present in same molecule
- (2) It proceed by cyclic transition state.
- (3) Overall it is syn elimination.
- (4) Hoffmann is major product as it is obtain by least hindered site/cyclic transition state.
- (5) No rearrangement.

Example of E_c/E_i**Pyrolysis of Ester :****1.8.2 Physical properties of chloroform**

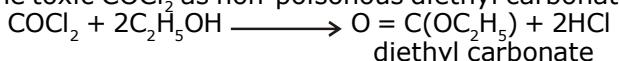
Chloroform is a colourless, heavy liquid which has sweetish, sickly odour and taste. It boils at 334° K and is slightly soluble in water. It is heavier than water. As inhaling of the vapours of chloroform induces unconsciousness therefore it can be used as an anaesthetic agent for surgery.

1.8.3 Chemical properties of chloroform

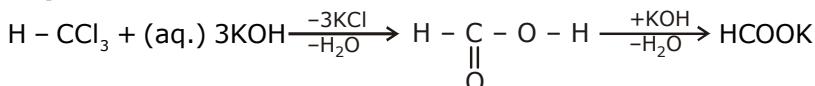
1. Action of sun light and air



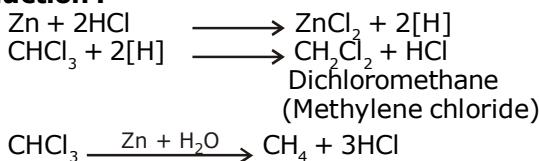
As chloroform is used for anaesthetic purposes, therefore in order to maintain a high purity of chloroform, this reaction can be avoided by storing it in dark bottles, completely filled upto brim. The use of dark bottles (brown or blue) cuts off active light radiations and filling upto brim keeps out air. Apart from this a small amount of ethanol (1%) is usually added to bottles of chloroform. Addition of a little ethanol fixes the toxic COCl_2 as non-poisonous diethyl carbonate.



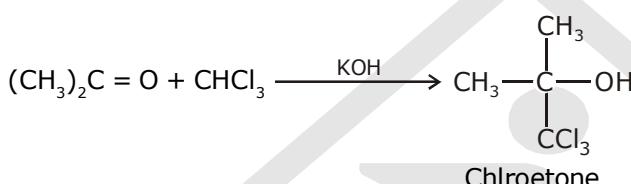
2. Hydrolysis :



3. Reduction :



4. Reaction with acetone :



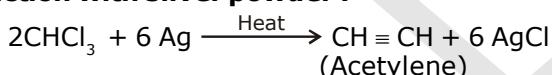
Use : Chloretone is used as hypnotic (a sleep inducing) drug.

5. Reaction with nitric acid

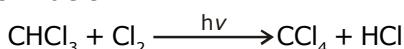


Use : Chloropicrin is used as an insecticide and war gas.

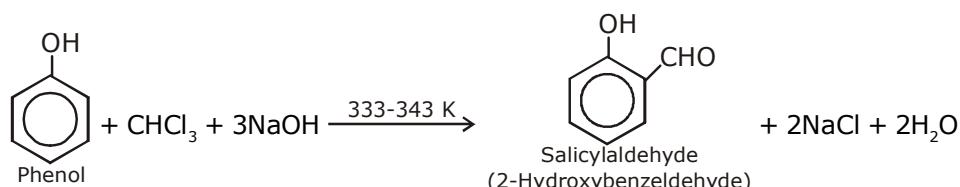
6. Reaction with silver powder :



7. Chlorination :

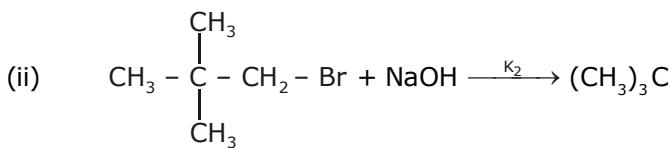
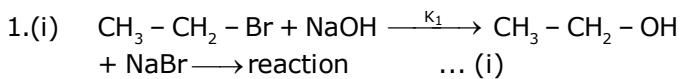


8. Reimer-Tiemann reaction:



1.8.4 Uses of chloroform

1. As solvent in oils and varnishes
2. As preservative for anatomical specimens
3. As laboratory reagent
4. As an anaesthetic

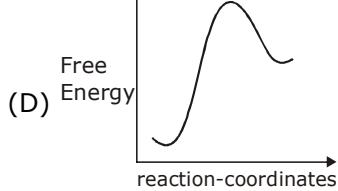
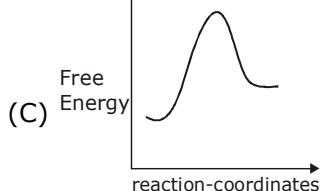
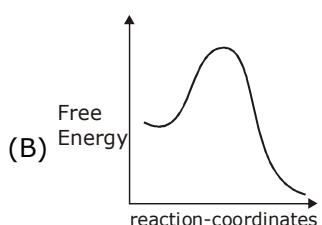
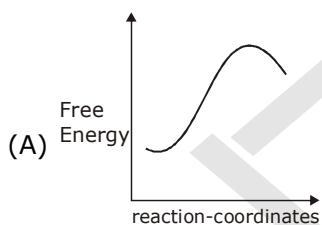
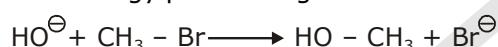
EXERCISE – I**JEE MAIN**

K_1 & K_2 are rate constant for above reaction
correct relation is

(A) $K_1 = K_2$ (B) $K_1 > K_2$
 (C) $K_1 < K_2$ (D) $K_1 \ll K_2$

Sol.

2. Free energy profile for given reaction is

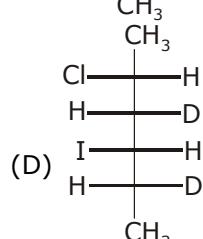
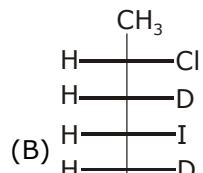
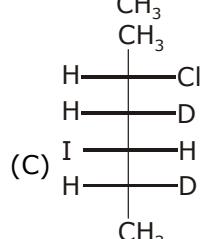
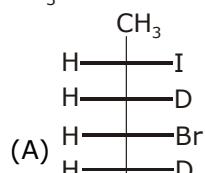
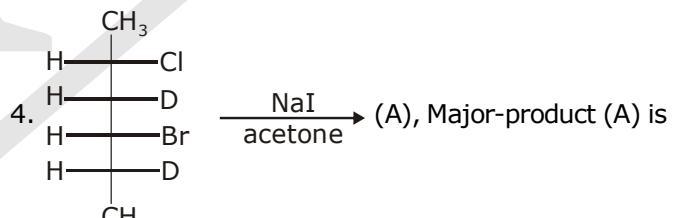


Sol.

3. Rate expression for reaction given in Que (2) is

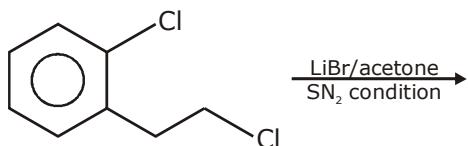
(A) rate = $K[\text{CH}_3 - \text{Br}]$
 (B) rate = $K[\text{HO}^\ominus][\text{CH}_3 - \text{Br}]$
 (C) rate = $K[\text{HO}^\ominus]$
 (D) rate = $K[\text{HO}^\ominus]^2 [\text{CH}_3 - \text{Br}]$

Sol.



Sol.

5.



(A), Product (A) is

(A)

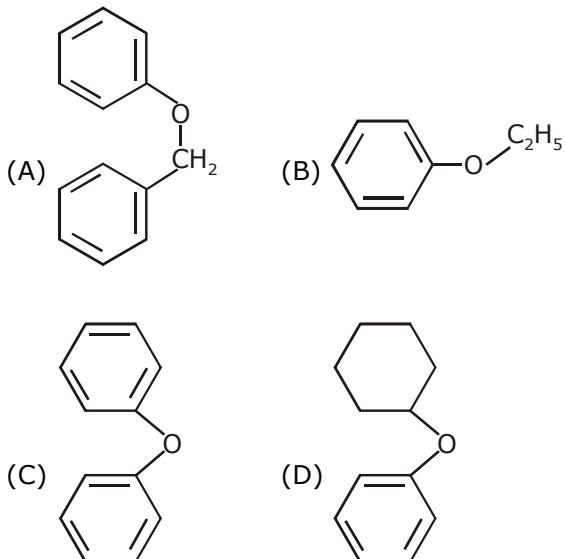
(B)

(C)

(D)

Sol.

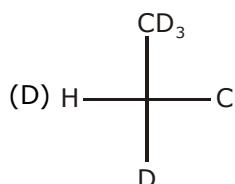
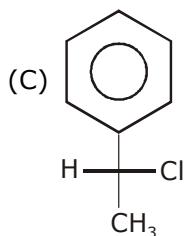
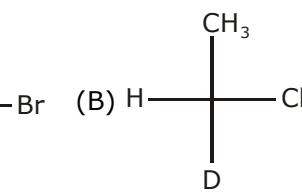
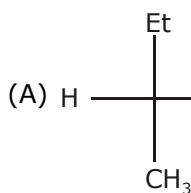
6. Which of the following ethers is unlikely to be cleaved by hot conc. HBr ?

**Sol.**

7. The reaction of $\text{CH}_3\text{OC}_2\text{H}_5$ with one mole HI gives
 (A) CH_3OH (B) $\text{C}_2\text{H}_5\text{OH}$
 (C) $\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH}$ (D) $\text{C}_2\text{H}_5\text{I} + \text{CH}_3\text{OH}$

Sol.

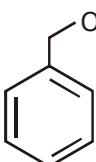
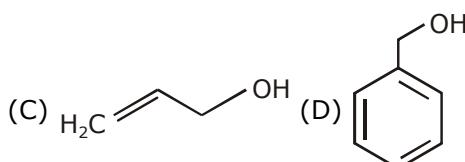
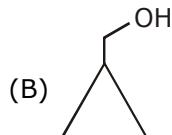
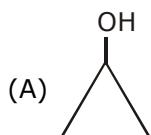
8. Under identical conditions, solvolysis of which of the following substrates would lead to maximum racemization?

**Sol.**

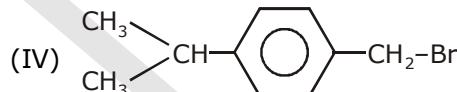
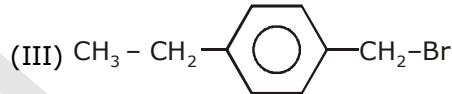
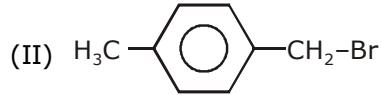
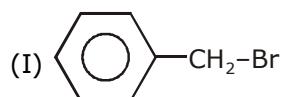
9. The reaction of SOCl_2 on alkanols to form alkyl chlorides gives good yields because
 (A) Alkyl chlorides are immiscible with SOCl_2
 (B) The other products of the reaction are gaseous and escape out
 (C) Alcohol and SOCl_2 are soluble in water
 (D) The reaction does not occur via intermediate formation of an alkyl chloro sulphite

Sol.

10. Which of the following alcohol shows fastest reaction with HI?

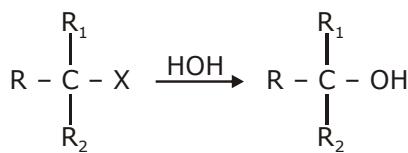
**Sol.**

11. Arrange the following compounds in order of decreasing rate of hydrolysis for $\text{S}_{\text{N}}1$ reaction

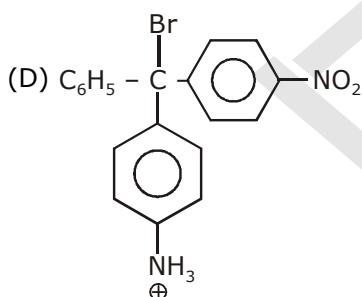
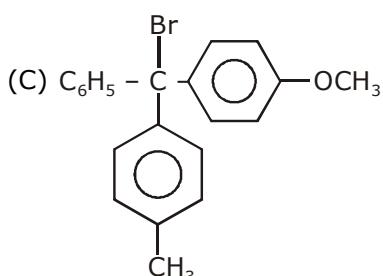
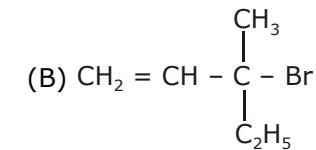
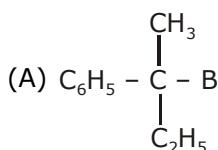
**Sol.**

(A) II > III > IV > I (B) IV > III > II > I
 (C) III > IV > II > I (D) I > II > III > IV

12. For the given reaction ;

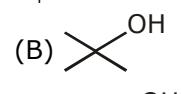
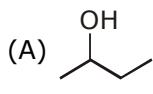


Which substrate will give maximum racemisation

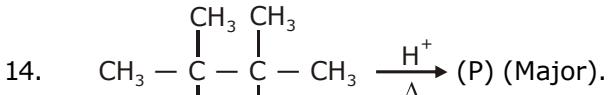


Sol.

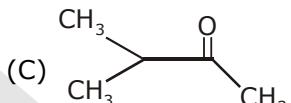
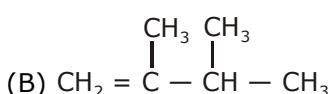
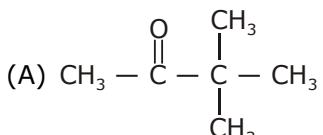
13. Which of these dehydrates most readily when reacts with conc. H_3PO_4 .



Sol.

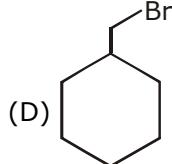
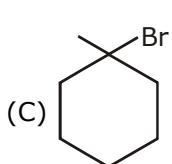
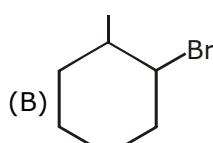
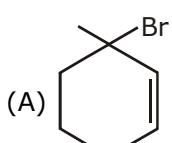


Major product (P) is :



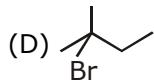
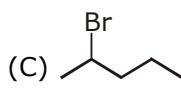
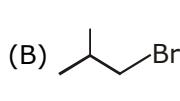
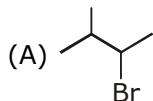
Sol.

15. Which of following halides gives fastest elimination reaction when it is treated with alcoholic KOH.

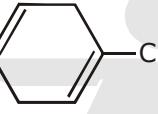
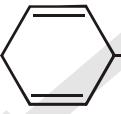


Sol.

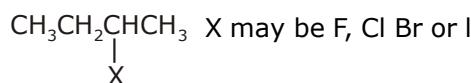
16. Which alkyl bromide will yield only one alkene upon E2 elimination?

**Sol.**

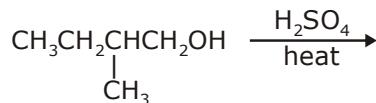
17. which is most easily dehydrohalogenated?

(A) I
(C) III(B) II
(D) All with same ease**Sol.**

18. Correct order of yield of Hofmann alkene in following reaction will be

(A) F > Cl > Br > I
(B) I > Br > Cl > F
(C) Cl > F > Br > I
(D) I > Br > F > Cl**Sol.**

19. Predict the major product of the following reaction :



(A) $\text{CH}_3\text{CH}_2\text{C} = \text{CH}_2$
(B) $\text{CH}_3\text{CH} = \text{C}(\text{CH}_3)_2$
(C) $\text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3$
(D) $(\text{CH}_3)_2\text{CHCH} = \text{CH}_2$

Sol.

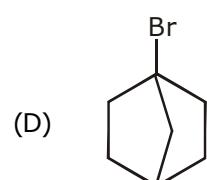
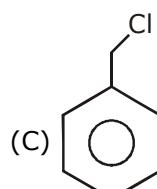
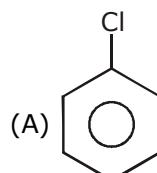
20.

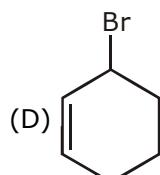
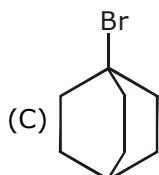
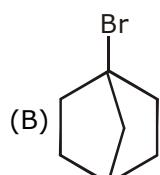
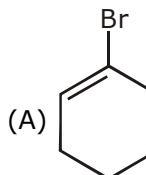
having α H
(A) 12 α H
(C) 4 α H

(B) 8 α H
(D) 11 α H

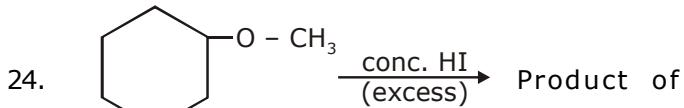
Sol.

21. Which of the following compound will not undergo Nucleophilic substitution reaction.

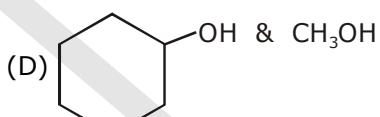
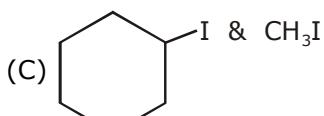
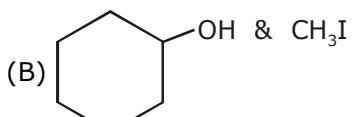
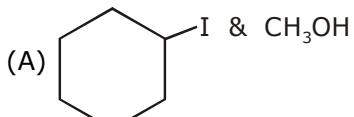
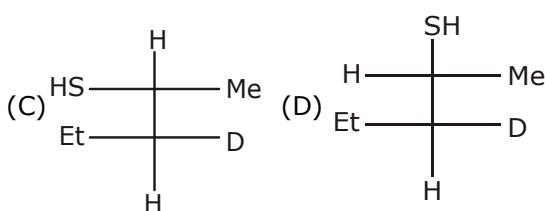
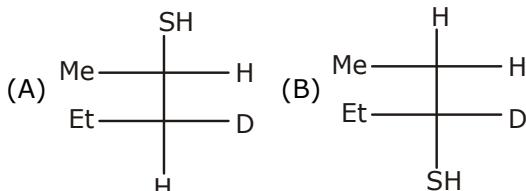
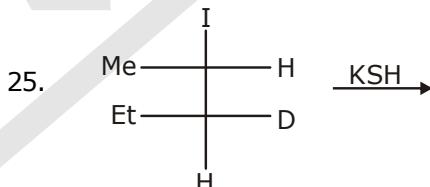


Sol.22. Rate of S_N2 will be negligible in**Sol.**23. Statement 1 : On moving 1° to 3° alkyl haliderate of E_2 increases while rate of S_N2 decreases
Statement 2 : E_2 reaction give element effect
respect to halogen.(A) Statement-1 is true, statement-2 is true and
statement -2 is correct explanation for statement-
1.(B) Statement-1 is true, statement-2 is true
and statement-2 NOT the correct explanation
for statement-1

(C) Statement :1 is true, statement-2 is false.

(D) Statement : 1 is false, statement -2 is
true**Sol.**

above reaction is

**Sol.**

Sol.

26. S_N1 is a two-step reaction. For each step, there has to be a transition state. Which of the following structures represent correctly the transition state of first step

(A) $[R^{\delta+} \dots L^{\delta-}]$ (B) $[R^{\delta-} \dots L^{\delta+}]$
 (C) $[R^{\delta+} \dots Nu^{\delta-}]$ (D) $[R^{\delta-} \dots Nu^{\delta+}]$

Sol.

27. Which one of the following compounds will give enantiomeric pair on treatment with HOH?

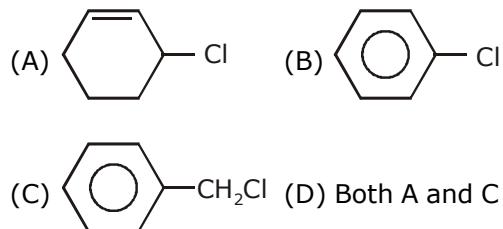
(A) $C_6H_5 - C(C_2H_5)_2 - I$ (B) $CH_3 - C(CH_3)_2 - Br$
 (C) $C_6H_5 - C(H) - Br$ (D) $C_2H_5 - C(CH_3) - Br$

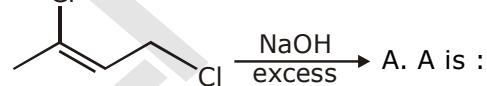
Sol.

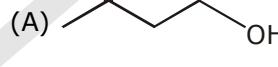
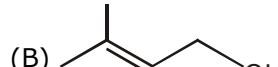
28. Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism
 (A) C_6H_5Cl (B) $Cl - CH_2 - CH = CH_2$
 (C) $(C_6H_5)_3CCl$ (D) $C_6H_5CH_2Cl$

Sol.

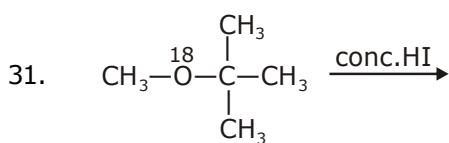
29. Which will give white ppt. with $AgNO_3$?

**Sol.**

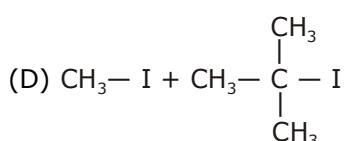
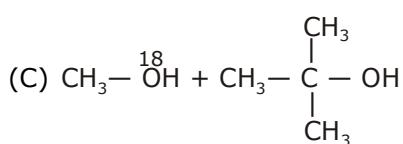
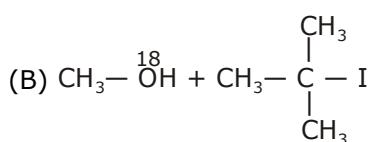
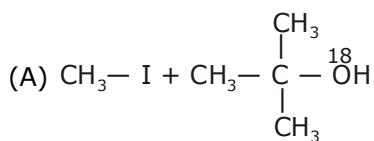
30. 

(A) 
 (B) 
 (C) 
 (D) 

Sol.

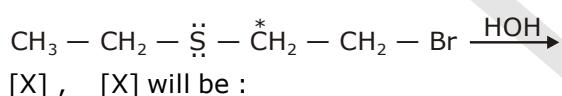


Products of above reaction is



Sol.

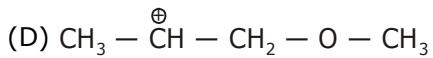
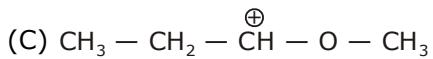
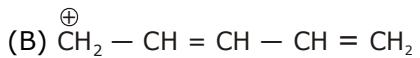
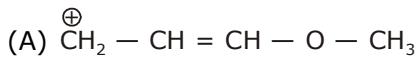
32. In the given reaction :



- (A) $\text{CH}_3-\text{CH}_2-\text{S}-\overset{*}{\text{CH}}_2-\text{CH}_2-\text{OH}$
- (B) $\text{CH}_3-\text{CH}_2-\text{S}-\text{CH}_2-\overset{*}{\text{CH}}_2-\text{OH}$
- (C) 1 : 1 mixture of (A) and (B)
- (D) 2 : 1 mixture of (A) and (B)

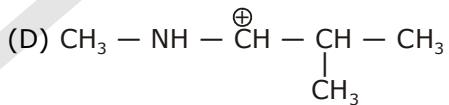
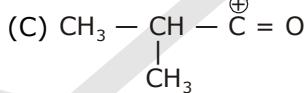
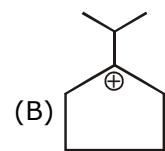
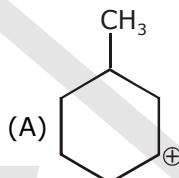
Sol.

33. Which of the following carbocation is most stable.



Sol.

34. Which of the following carbocation will undergo rearrangement ?

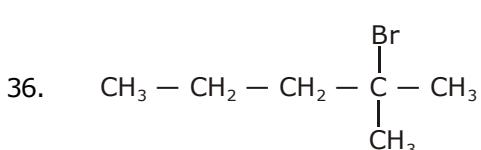


Sol.

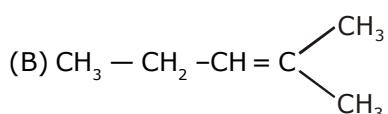
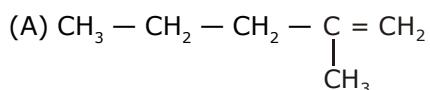
35. Which of following is dehydrating agent ?



Sol.

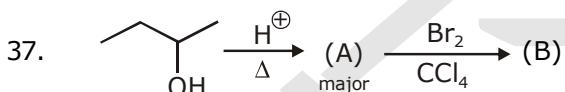


Identify all possible product obtained by E_2 reaction?



(C) both (A) and (B)
(D) none of these

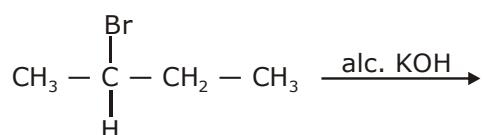
Sol.



Product (B) is
(A) meso
(B) Racemic
(C) Diastereomer
(D) optically active single products

Sol.

38. Major product of the reaction is

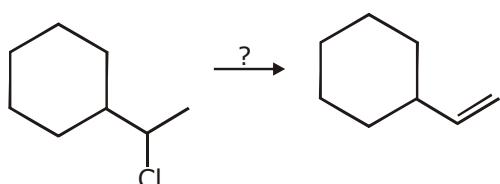


(A) Butene-1 (B) Trans-2-butene
(C) cis-2-butene (D) Butyne-1

Sol.

39.

In order to accomplish the following conversion, what reagent and conditions would be required?

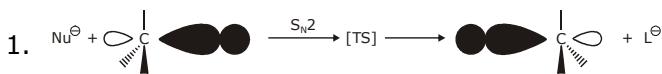


(A) Cold sodium hydroxide
(B) Hot conc. sodium hydroxide
(C) Potassium t-butoxide and heat
(D) Hot water

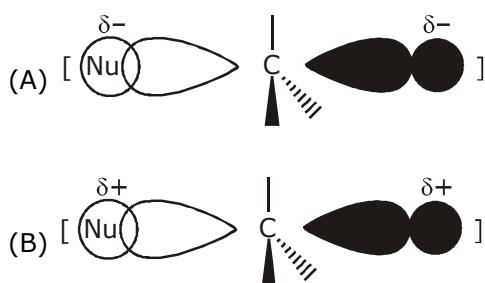
Sol.

EXERCISE - II

JEE ADVANCED (OBJECTIVE)



Which of the following figures represent correctly the structure of transition state in this reaction?



(C) either (A) or (B) depending upon situation
(D) none of these

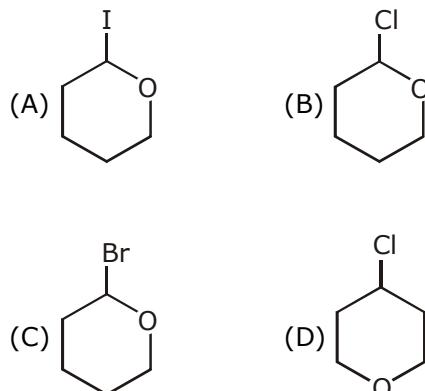
Sol.

2. From each of the following pairs select the compound that will react faster with sodium iodide in acetone

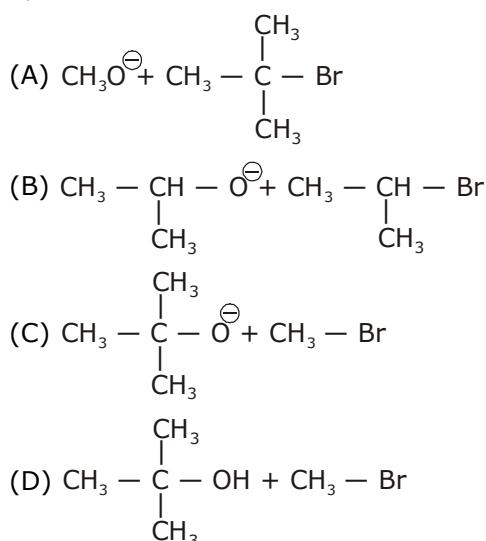
(a) 2-Chloropropane or 2-bromopropane
I II
(b) 1-Bromobutane or 2-bromobutane
I II
(A) (a)-I, (b)-I (B) (a)-I, (b)-II
(C) (a)-II, (b)-I (D) (a)-II, (b)-II

Sol.

3. Which of the following compound will be most reactive for $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions

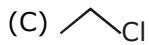
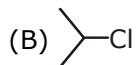
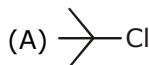
**Sol.**

4. Best method for preparation of
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{O}-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ by williamson's ether synthesis is



Sol.

5. In the acid catalyzed dehydration of alcohols to alkenes, the intermediate species formed is
 (A) Free radical (B) Carbocation
 (C) Carbanion (D) Carbene

Sol.**Comprehension (Q.6 to 9)**

6. Most reactive towards $\text{S}_{\text{N}}1$ reaction

Sol.

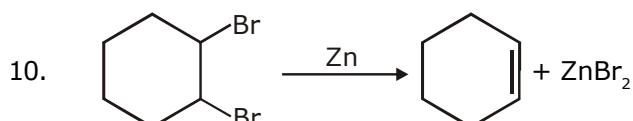
7. Most reactive towards $\text{S}_{\text{N}}2$ reaction ?

Sol.

8. Most reactive towards E_2 reaction ?

Sol.

9. Most reactive towards E_1 reaction ?

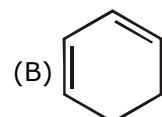
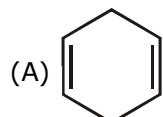
Sol.

This reaction is a case of

(A) α -elimination (B) β -elimination
 (C) γ -elimination (D) none of these

Sol.

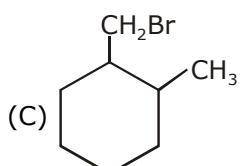
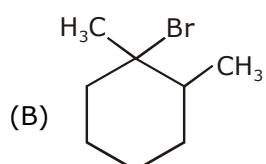
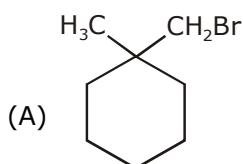
The major products obtained when this substrate is subjected to E_2 reaction will be



(C) both (A) and (B) (D) none of these

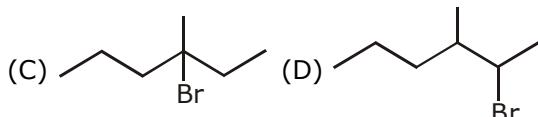
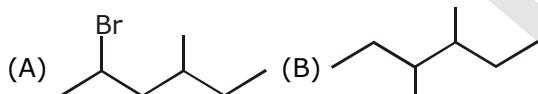
Sol.

12. Which of following cannot undergo an E2 reaction?



Sol.

13. Which alkylbromide will yield 3-methyl-1-hexene as the major product upon treatment with potassium t-butoxide in t-butyl alcohol (solvent) ?

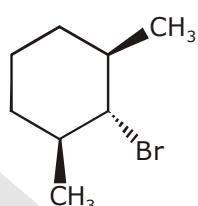


Sol.

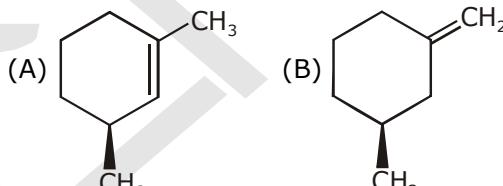
14.

Total number of SN_1 products of given compound are

Sol.

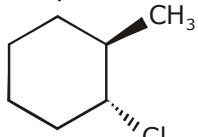


The major product obtained when this substrate is subjected to E2 reaction will be

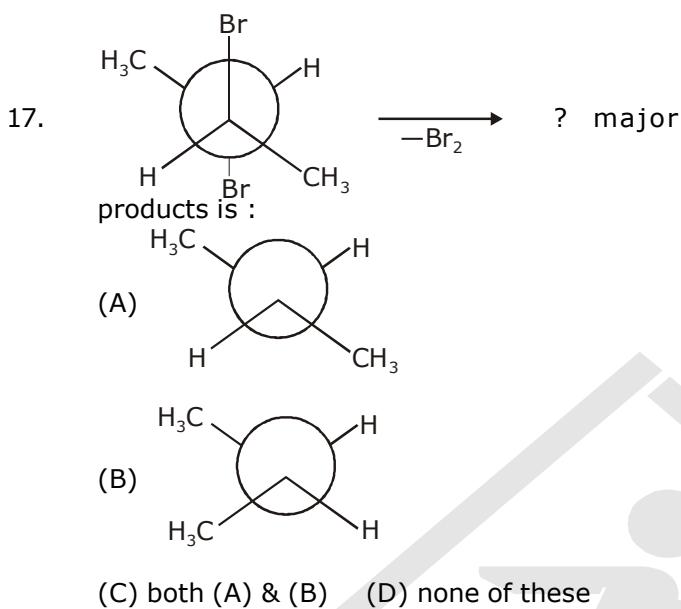
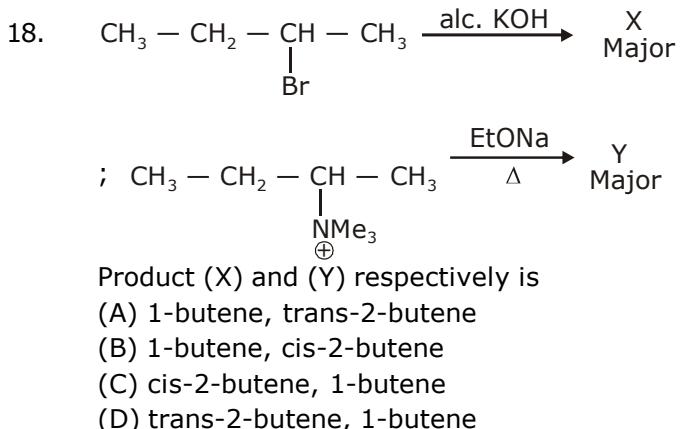


Se

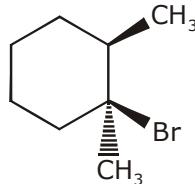
16. If the following E2 reaction proceeds through an anti-periplanar transition state, what products are expected ?



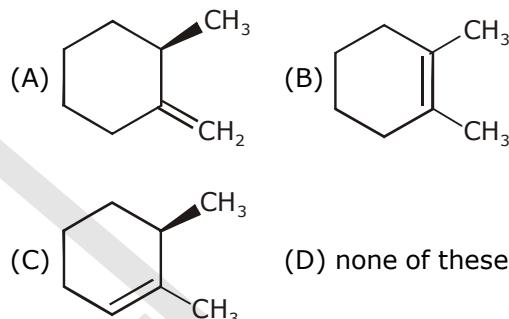
(A) Only 3-methylcyclohexene
(B) Only 1-methylcyclohexene
(C) The major product is 3-methylcyclohexene
and the minor product is 1-methyl cyclohexene
(D) The major products is 1-methylcyclohexene
and the minor product is 3-methyl cyclohexene

Sol.**Sol.****Sol.**

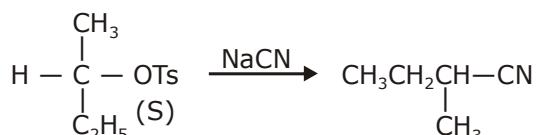
19.



The major product obtained when this substrate is subjected to E1 reaction will be

**Sol.**

20. Consider the given reaction

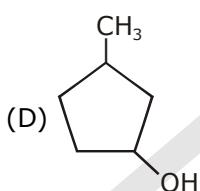
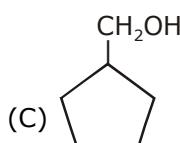
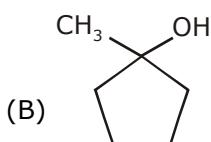
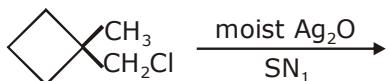
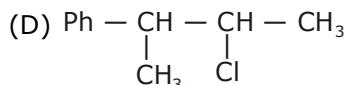
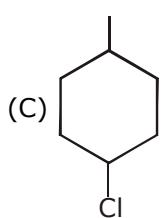
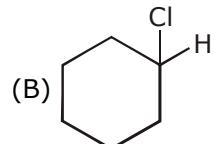
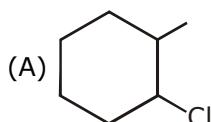
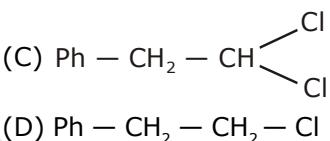
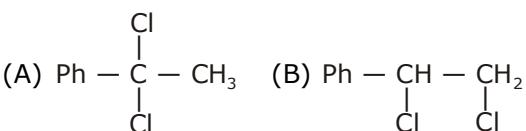


Which of following statement are correct for above reaction.

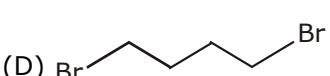
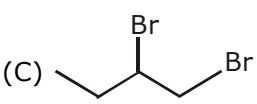
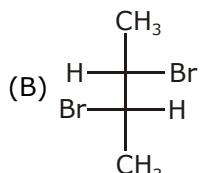
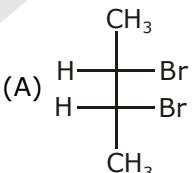
(A) Product formation takes place due to the breaking of O—Ts
 (B) The reaction $\text{S}_{\text{N}}2$
 (C) The reaction is $\text{S}_{\text{N}}1$
 (D) Configuration of product is (R)

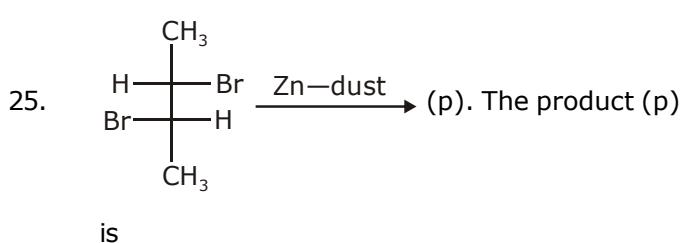
Sol.

21. Which are possible products in following

**Sol.**22. $\text{S}_{\text{N}}1$ & $\text{S}_{\text{N}}2$ product are same in (excluding steroisomer)**Sol.**23. $\text{Ph} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3 \xrightarrow{\text{PCl}_5}$ product are**Sol.**24. (p) $\xrightarrow{\text{Zn-dust}}$

compound (p) is

**Sol.**



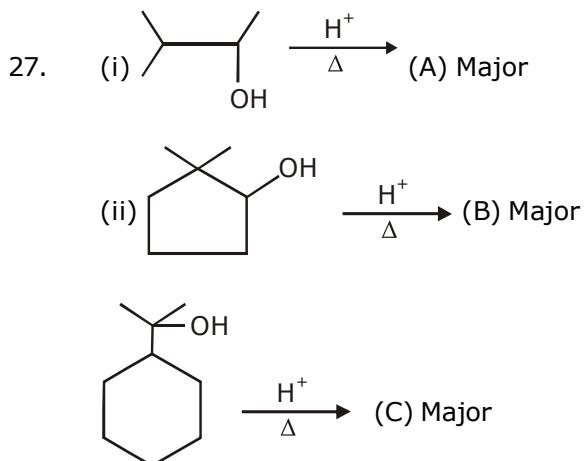
(A) 

(B) 

(C) 

(D) 

Sol.



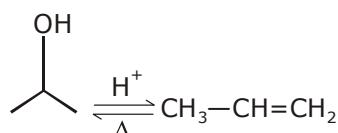
Total number of α -hydrogen in A + B + C is
(A) 23 (B) 25
(C) 37 (D) 29

Sol.

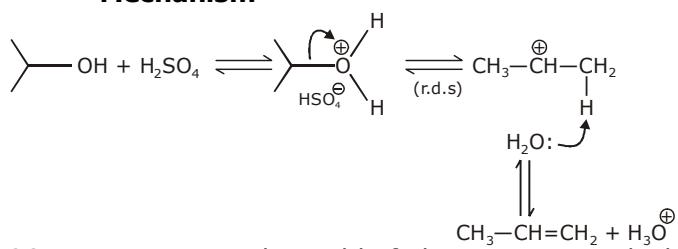
Paragraph for Question Nos. 11 to 13 (3 questions)

2

Dehydration require an acid catalyst to protonate the hydroxy group of the alcohol and convert it into good leaving group. Loss of water followed by a loss of a proton, given the alkene an equilibrium is established between reactants and products.



Mechanism

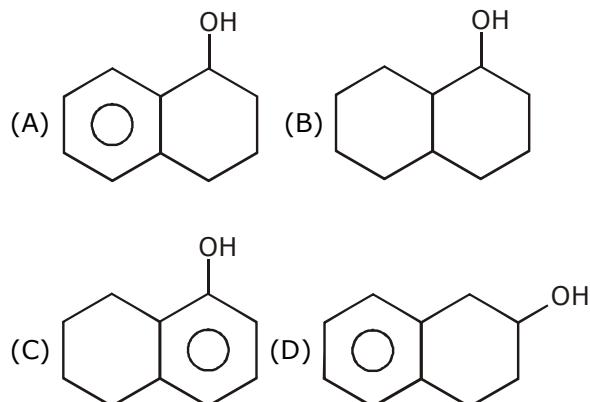


26. To improve the yield of above reaction which of following is correct.

(A) High temperature
(B) Distillation
(C) Addition of H_2O
(D) Both (A) and (B)

Sol.

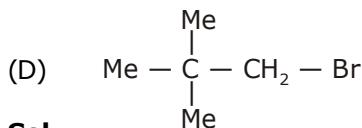
28. Which alcohol is most reactive towards dehydration of alcohols in acids catalyzed reaction.



Sol.

MATRIX MATCH**29. Column I****Primary alkyl bromide**

(A) $\text{CH}_3 - \text{CH}_2 - \text{Br}$
 (B) $\text{Me} - \text{CH}_2 - \text{CH}_2 - \text{Br}$
 (C) $\text{Me} - \text{CH} - \text{CH}_2 - \text{Br}$
 |
 Me

**Sol.****Column II** **$\text{S}_{\text{N}}2$ relative rate**

(P) 10^{-5}
 (Q) 10^{-2}
 (R) 0.8

(S) 1

30. Column I**Alkyl-P-toluene sulfonate**

(A) $\text{CH}_3 - \text{CH}_2 - \text{OTs}$
 (B) $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{OTs}$
 (C) $\text{Ph} - \text{CH}_2 - \text{OTs}$.
 (D) $\text{Ph} - \text{CH} - \text{OTs}$
 |
 Ph
 (E) $\text{Ph}_3\text{C} - \text{OTs}$.

Sol.**Column II****Ethanolysis relative**

(P) 10^{10}
 (Q) 10^5
 (R) 400
 (S) 35
 (T) 1

31. Substrate

(A) $\text{CH}_3 - \text{CH}_2 - \text{Br}$
 (B) $(\text{CH}_3)_2\text{CH} - \text{Br}$
 (C) $(\text{CH}_3)_3\text{CBr}$

Sol. **E_2 elimination**

(P) 1
 (Q) 80
 (R) 100

 $\text{S}_{\text{N}}2$ — substitution

(W) ≈ 0
 (X) 20
 (Y) 90

32.	Reaction	Reaction rate of reaction	
(A)	$\text{HO}^\ominus + \text{R}-\text{CH}_2-\text{I} \longrightarrow$	(P)	1
(B)	$\text{HO}^\ominus + \text{R}-\text{CH}_2-\text{Br} \longrightarrow$	(Q)	200
(C)	$\text{HO}^\ominus + \text{R}-\text{CH}_2-\text{Cl} \longrightarrow$	(R)	10,000
(D)	$\text{HO}^\ominus + \text{R}-\text{CH}_2-\text{F} \longrightarrow$	(S)	30,000

Sol.

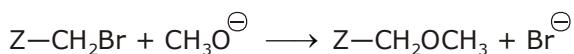
33.	Column I Alkyl-bromide	Column II Relative rate of SN^1
(A)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	(P) 1
(B)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	(Q) 11.6
(C)	$\text{CH}_3-\text{CH}_2-\text{Br}$	(R) 1,200,000

Sol.

34.	Column I Solvent	Column II Relative rate of SN^1
(A)	100% water	(P) 1200
(B)	80% water + 20% ethanol	(Q) 400
(C)	50% water + 50% ethanol	(R) 60
(D)	20% water + 80% ethanol	(S) 10
(E)	100% ethanol	(T) 1

Sol.

35. Match List-I with List II for given $S_{N}2$ reaction & select the correct answer from the codes given below

**List I****List II (relative reactivity)**

(A) H—	(P) 0.1
(B) CH_3-	(Q) 3
(C) C_2H_5-	(R) 1
(D)	(S) 100

Sol.

36. Match List I with List II and select the correct answer from codes given below.

List I**List II**

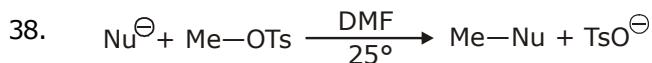
(A) $\text{CH}_3 - \text{O} - \text{SO}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{O}^-$	(P) $\text{CH}_3 - \text{CH}_2 - \text{PH}_2$
(B) $\text{CH}_3 - \text{CH}_2 - \text{I} + \text{PH}_3$	(Q) $\text{CH}_2 - \text{O} - \text{C}_2\text{H}_5$
(C) $\text{HC} \equiv \text{C}^{\ominus} \text{Na} + \text{CH}_3 - \text{CH}_2 - \text{Br}$	(R) $\text{CH}_3 - \text{O} - \text{CH}_3$
(D) $\text{CH}_3 - \text{Cl} + \text{CH}_3 - \text{O}^-$	(S) $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$

Sol.

37. Column I and Column II contains **four** entries each. Entries of column I are to be matched with some entries of columnII. One or more than one entries of column I may have the matching with the same entries of column II and one entry of column-I may have one or more than one matching with entries of column II.

Column I**Column II**

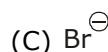
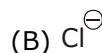
(A)		(P) S_N2 reaction
(B)		(Q) E_1 reaction
(C)		(R) E_2 reaction
(D)		(S) S_N1 reaction

Sol.

This is a S_N2 reaction where nucleophile attack Me—OTs in the rate determining step to give the product. Rate of this reaction increases with concentration as well as nucleophilicity of the nucleophile . Match the column I with column II for the above reaction.

Column I

(Nucleophile)

**Column II**

(Relative rate)

(P) 3.25

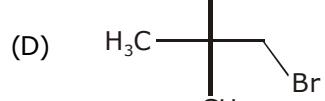
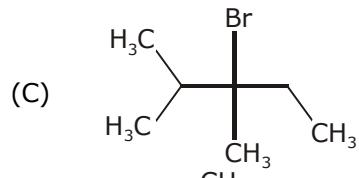
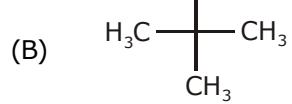
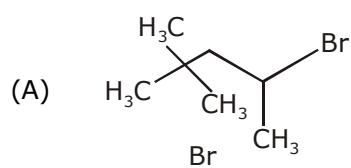
(Q) 6.25

(R) 1.0

(S) 7.75

Sol.

39. Match List I with List II (no. of structural isomers produced in $\beta\text{-E}_2$ elimination) and select the correct answer.

List I**List II**

(i) Three

(ii) Zero

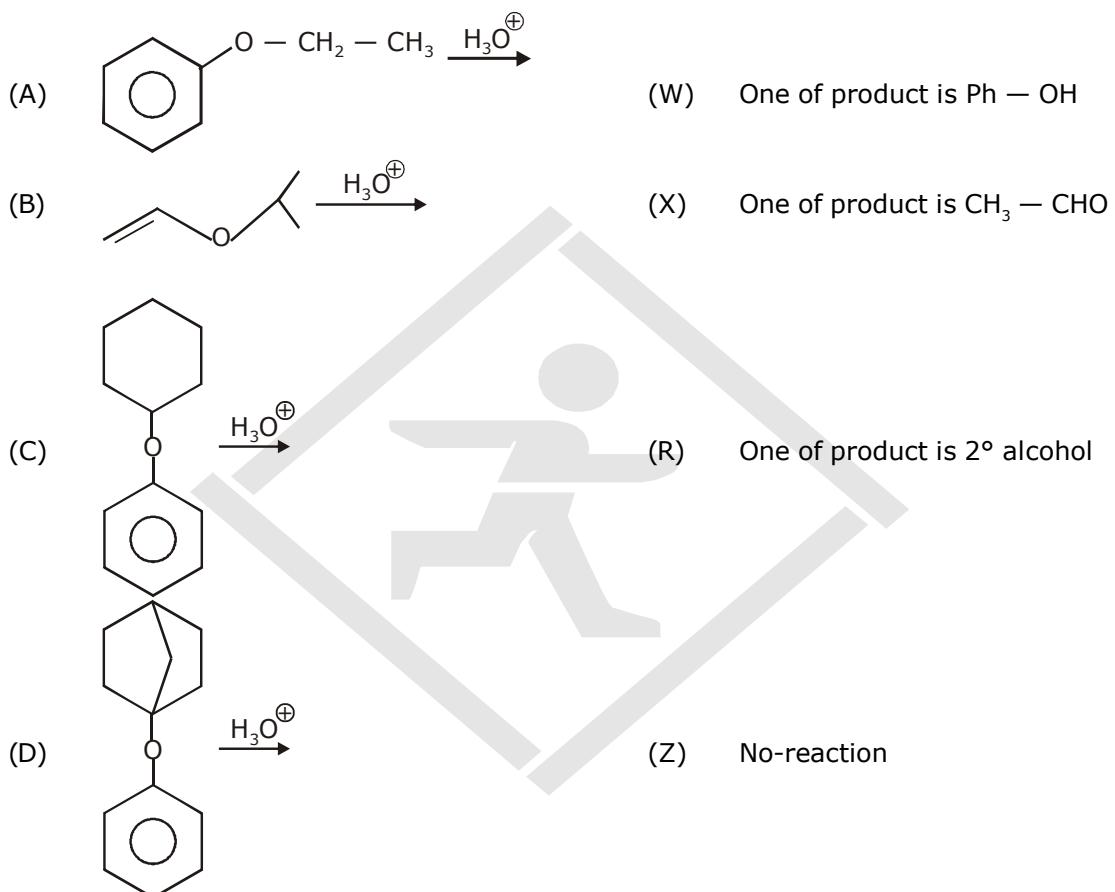
(iii) One

(iv) Two

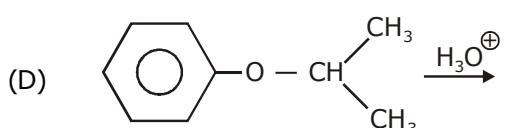
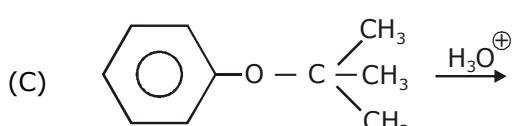
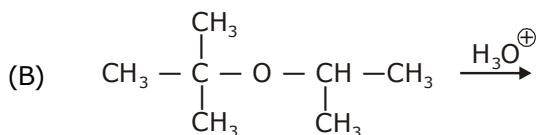
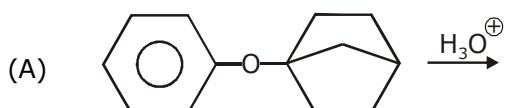
(A) (a)(b)(c)(d)
(B) (i)(ii)(iv)(iii)
(C) (iv)(iii)(ii)(i)(D) (a)(b)(c)(d)
(B) (iv)(iii)(i)(ii)
(D) (i)(iii)(iv)(ii)

Sol.

40. Match the column

**Sol.**

41.

Column I**Column II**

(P) No reaction

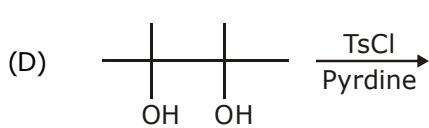
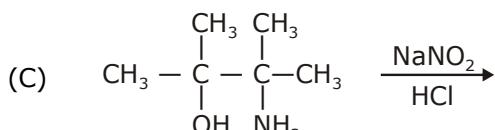
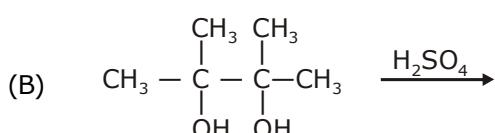
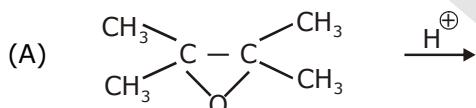
(Q) $\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$ is one of the product of the reaction

(R) is one the product
Product of the reaction

(S) $\begin{array}{c} CH_3 \\ | \\ CH_3-CH-OH \\ | \\ CH_3 \end{array}$ is one the product
product of the reaction

Sol.

42.

Column I**Column II**

(P) Pinacol fashion reaction

(Q) Pinacolic Diazotization reaction

(R) Pinacol-Pinacolone reaction

(S) Product formed is $\begin{array}{c} O \\ || \\ CH_3-C-CH-CH_3 \\ | \\ CH_3 \end{array}$
(T) Semipinacol reaction

Sol.**43. Column I**

(A) Best leaving group
 (B) Best nucleophile in polar protic solvent
 (C) Best nucleophilic in polar aprotic solvent
 (D) Weakest base

Column II

(P) F^-
 (Q) Cl^-
 (R) Br^-
 (S) I^-

Sol.**44. Substitution Logistics :**

You were asked to run a series of reaction in the lab with different experimental conditions. Based on the experimental observation you gathered (listed below), indicate which mechanism this evidence supports. (Check the appropriate box to correspond to your answer.)

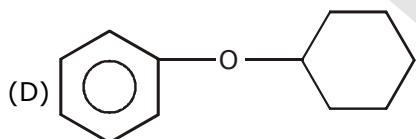
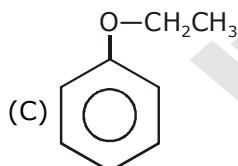
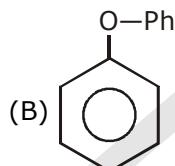
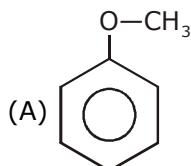
No.	Observation	SN1	SN2	Both
1	The rate of the reaction decreased when the concentration of the Nu is decreased.			
2	The rate of the reaction increased when the concentration of the RX was increased.			
3	The rate increased when the X was changed from Cl to I.			
4	The products showed a skeletal rearrangement.			
5	The product showed inversion of configuration.			
6	The Nu was changed from methoxide to isopropoxide and the rate decreased.			
7	The RX was changed from 2° alkyl halide to a 2° allyl halide and the increased.			
8	The solvent was switched from ethanol to acetone and the rate decreased.			

EXERCISE – III**JEE ADVANCED**

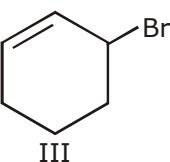
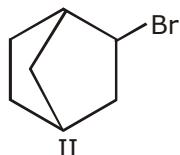
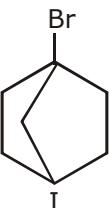
1. Which of the following reaction is not possible
 (A) $R - OH + NaBr \rightarrow R - Br + NaOH$
 (B) $R - OH + HBr \rightarrow R - Br + H_2O$
 (C) both reaction are possible
 (D) both reactions are not possible

Sol.

2. Which of the following compound will not undergo acid catalysed hydrolysis ?

**Sol.**

3.



S_N2 reactivity of these substrate, under identical conditions, will be in the order as

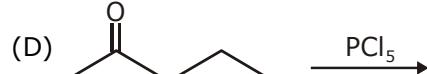
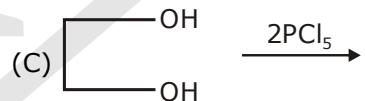
(A) I > II > III (B) III > II > I
 (C) III > I > II (D) II > III > I

Sol.

4.

A gem dichloride is formed in the reaction except

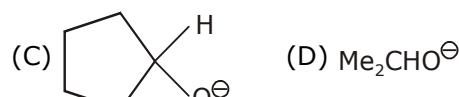
(A) CH_3CHO and PCl_5 (B) CH_3COCH_3 and PCl_5

**Sol.**

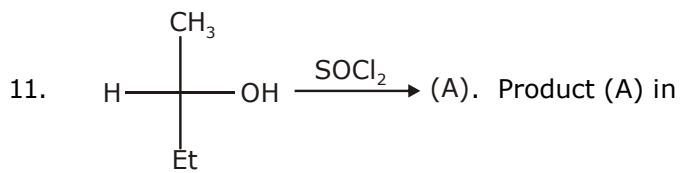
5.

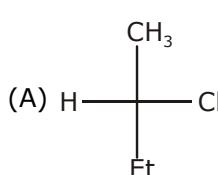
Which of the following nucleophile will show minimum reactivity towards S_N2 reaction

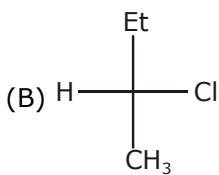
(A) Me_3CO^- (B) MeO^-

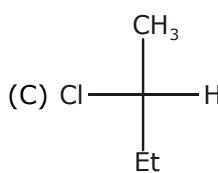


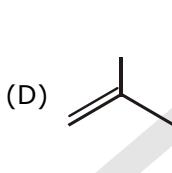
(D) Me_2CHO^-

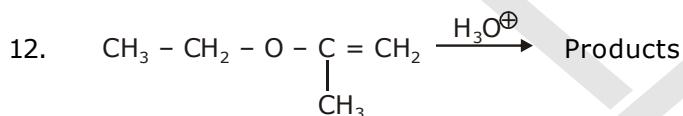
Sol.

(A) 

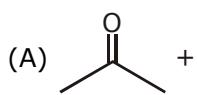
(B) 

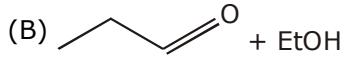
(C) 

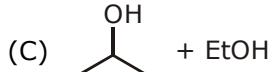
(D) 

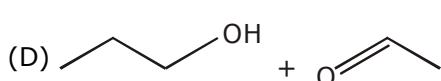
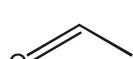
Sol.

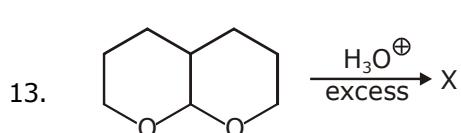
are

(A)  + EtOH

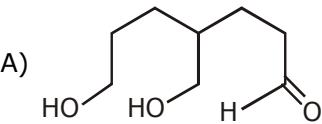
(B)  + EtOH

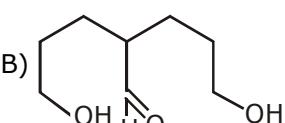
(C)  + EtOH

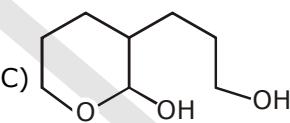
(D)  + 

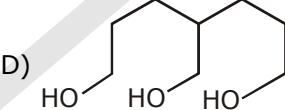
Sol.

Structure of X is

(A) 

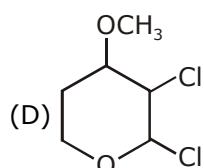
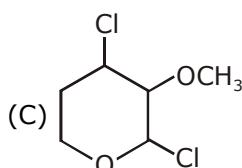
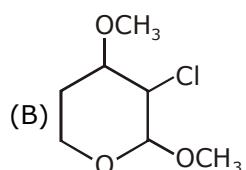
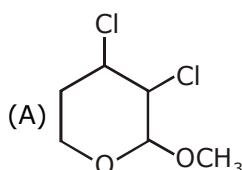
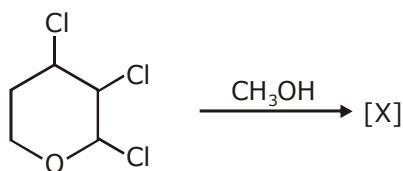
(B) 

(C) 

(D) 

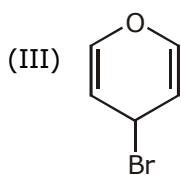
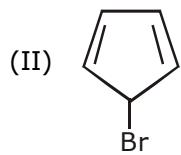
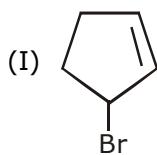
Sol.

14. In the given reaction :



Sol.

15. Among the bromides I-III given below, the order of reactivity is S_N1 reaction is

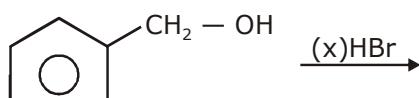


(A) III > I > II
(C) II > III > I

(B) III > II > I
(D) II > I > III

Sol.

16.

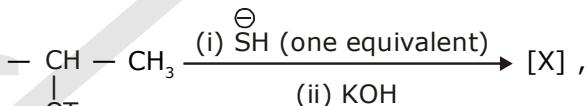


Value of (x) is
(A) 1
(C) 3

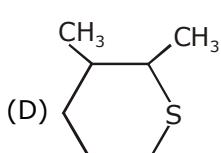
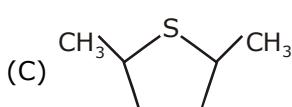
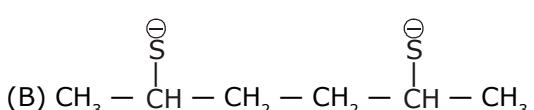
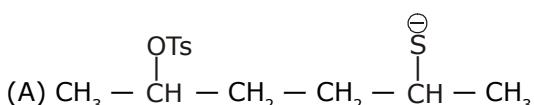
(B) 2
(D) 4

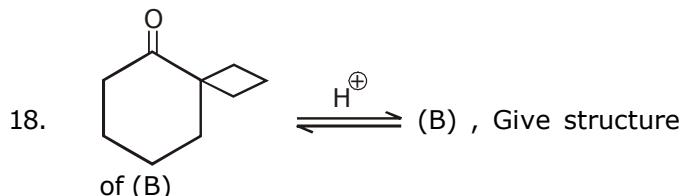
Sol.

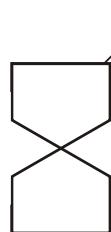
17. In the given reaction $\text{CH}_3 - \underset{\substack{| \\ \text{OTs}}}{\text{CH}} - \text{CH}_2 - \text{CH}_2$

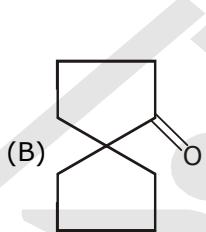


$[X]$ will be :

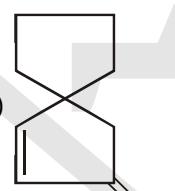


Sol.

(A) 

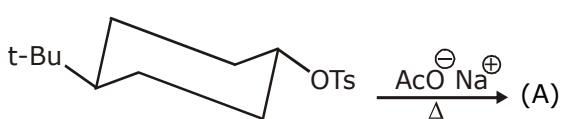
(B) 

(C) 

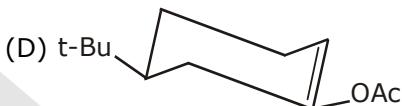
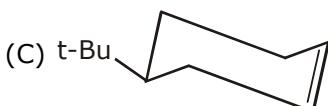
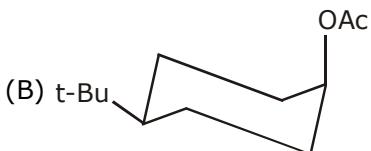
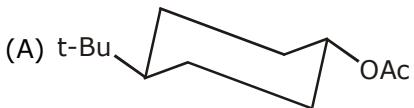
(D) 

Sol.

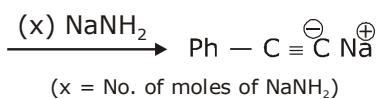
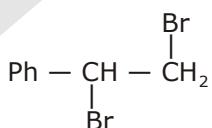
19.



Major-product (A) is

**Sol.**

20.

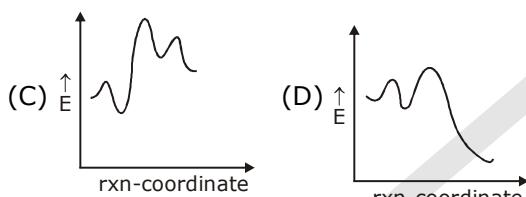
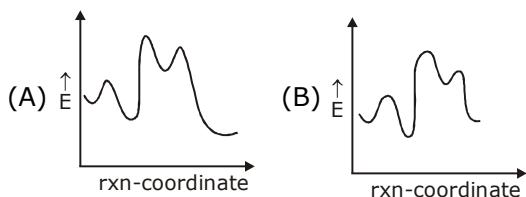
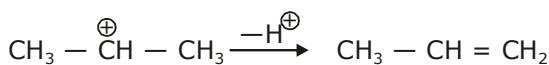
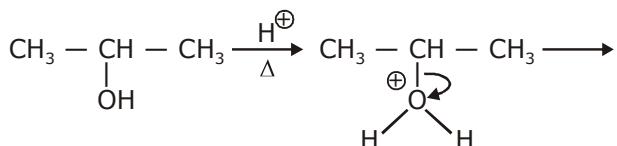


Value of x is

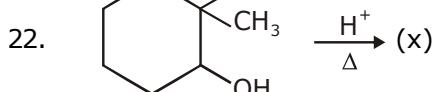
(A) 1 (B) 2
(C) 3 (D) 4

Sol.

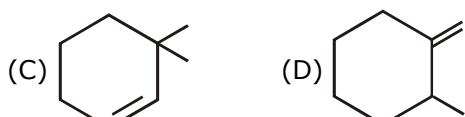
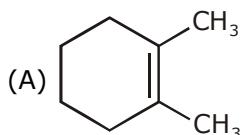
21. The energy profile of the given reactions.



Sol.

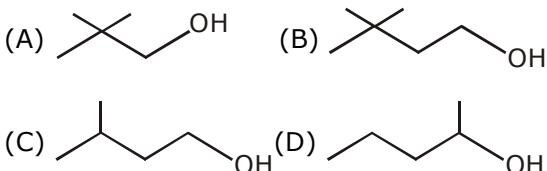


Major product (X) is

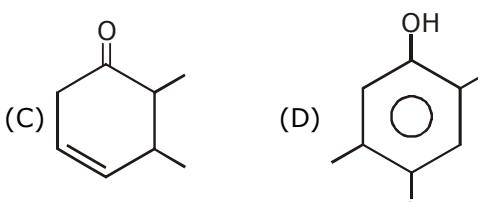
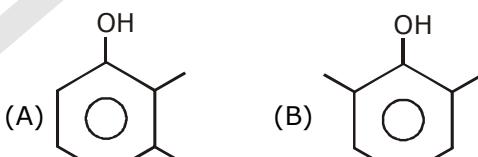
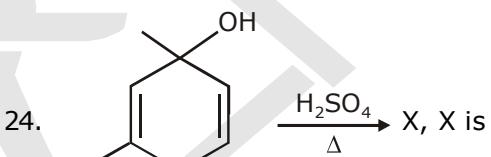


Sol.

23. Which of the following alcohols would be most likely to undergo dehydration with rearrangement by a process involving a methyl migration (methyl shift only) ?

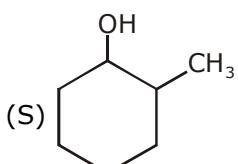
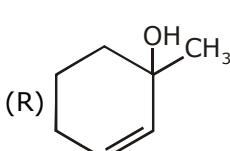
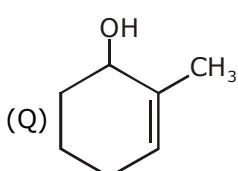
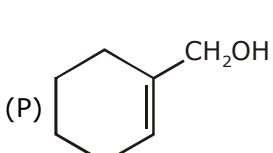


Sol.



Sol.

25. Rate of dehydration when given compound is treated with conc. H_2SO_4 .



(A) P > Q > R > S (B) Q > P > R > S
 (C) R > Q > P > S (D) R > Q > S > P

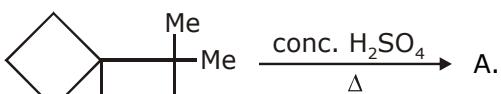
Sol.

Final product A is

(A)
 (B)
 (C)
 (D)

Sol.

27.



Product A is

(A)

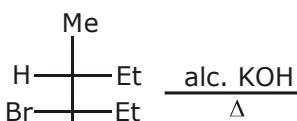
(B)

(C)

(D)

Sol.

28.



(A)
 (B)
 (C)
 (D)

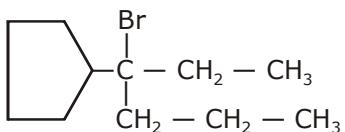
Sol.

29.

Most reactive towards acid-catalyzed hydrolysis is

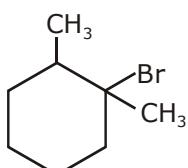
(A)
 (B)
 (C) EtOEt
 (D) EtOH

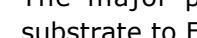
Sol.

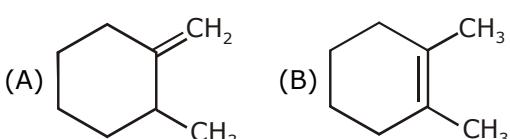


30.  Total number of products of combustion of this substrate is subjected to ESR (including stereoisomer) (A) 3 (B) 4 (C) 5 (D) 6

Sol.

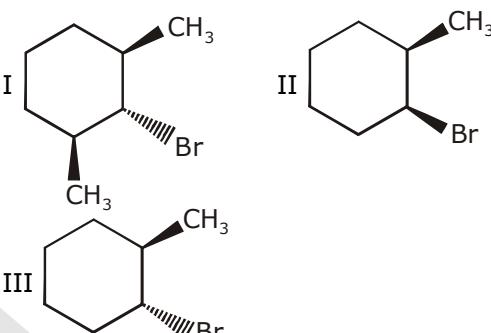


31. 
The major products obtained when this substrate to E2 reaction under the treatment of potassium tert-butoxide will be



- (C) both in equal proportions
- (D) none of these

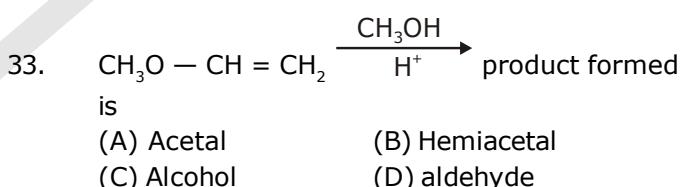
Sol.



Ease of β -dehydrobromination among these substrates under the treatment of strong base will be in the order as

(A) i > ii > iii (B) iii > ii > i
 (C) ii > i > iii (D) ii > iii > i

Sol.



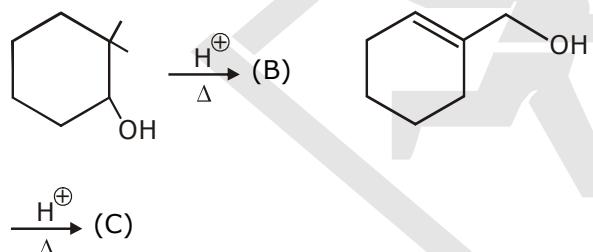
Sol.

34. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{C}} - \text{CH}_2 - \text{CH}_3$

Total number of $\text{SN}_1 + \text{E}_1$ products obtained will be -

Sol.

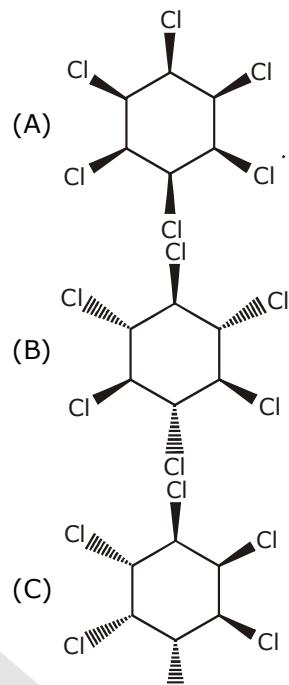
35. $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{CH}_3 \quad \text{OH} \end{array} \xrightarrow[\Delta]{\text{H}^+} (\text{A})$



Stability of product (A), (B), (C) is :
(A) C > B > A (B) A > B > C
(C) B > C > A (D) C > A > B

Sol.

36. Which of the following isomeric hexachlorocyclohexanes is least reactive in (β)-dehydrochlorination of treatment with strong base

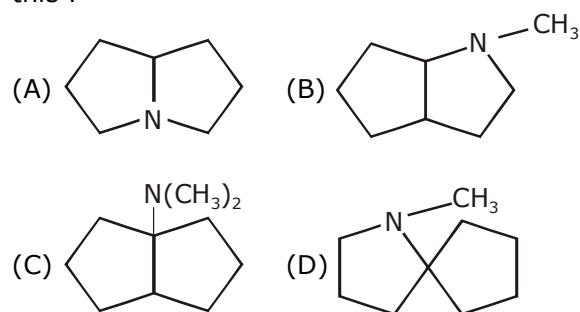


(D) all three are equally reactive

Sol.

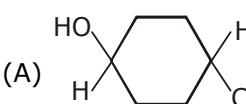
37. The nitrogen atom in each of the following tertiary amines may be removed as trimethylamine by repeated Hofmann eliminations (exhaustive methylation followed by heating with AqOH).

Which of the amines requires the greater number of Hofmann sequences to accomplish this?

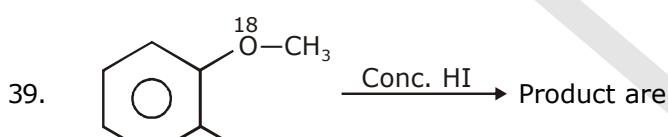


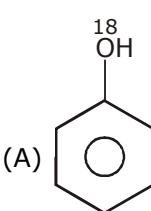
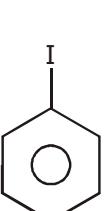
Sol.

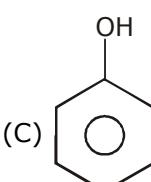
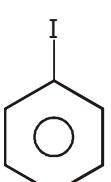
A is

(A)  (B) 

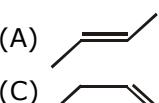
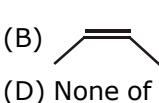
(C) both (D) 

Sol.

(A)  + CH₃I (B)  + CH₃¹⁸OH

(C)  + CH₃I (D)  + H₂O

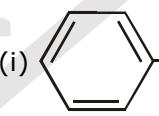
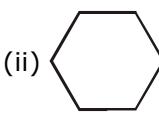
Sol.

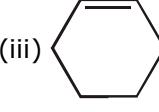
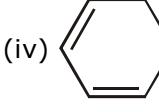
(A)  (B) 

(C)  (D) None of these

Sol.

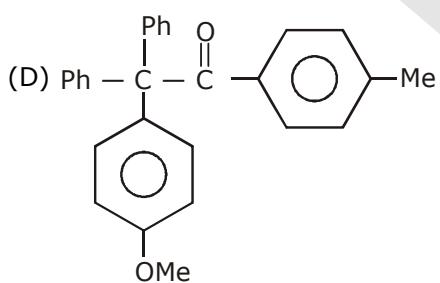
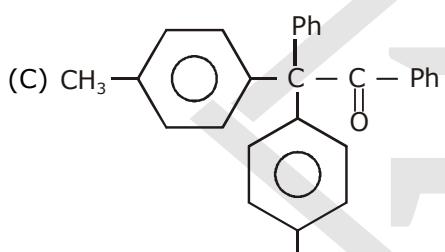
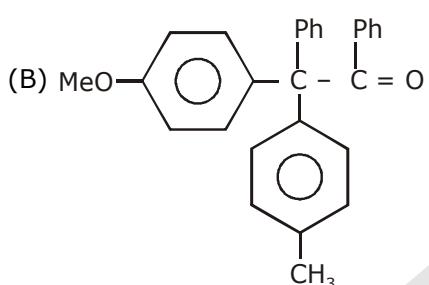
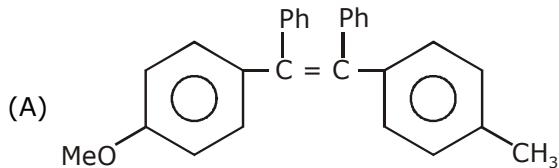
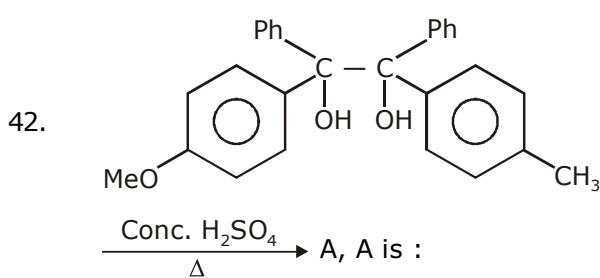
41. Among the given compounds, the correct dehydration order is :

(i)  (ii) 

(iii)  (iv) 

(A) i < ii < iii < iv (B) ii < iii < iv < i
 (C) i < iii < iv < ii (D) i < ii < iii = iv

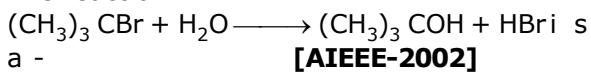
Sol.

**Sol.**

43. Which of the following expressions is the experimentally observed rate law for an E2 reaction of alkyl halide ?

- (A) Rate = $k[RX]$
- (B) Rate = $k [RX]^2$
- (C) Rate = $k[RX][\text{base}]$
- (D) Rate = $k[\text{base}]$

Sol.

EXERCISE – IV**LEVEL – I****PREVIOUS YEARS****JEE MAIN****Q.1** The reaction

- (A) Substitution reaction
- (B) Debromination reaction
- (C) Rearrangement reaction
- (D) Elimination reaction

Sol.**Q.2** The correct order of the thermal stability of hydrogen halides (H – X) is –

[AIEEE-2005]

- (A) HF > HCl > HBr > HI
- (B) HI > HBr > HCl > HF
- (C) HI > HCl < HF > HBr
- (D) HCl < HBr > HBr < HI

Sol.**Q.3** Tertiary alkyl halides are practically inert to substitution by S_N^2 mechanism because of –

[AIEEE-2005]

- (A) instability
- (B) insolubility
- (C) steric hindrance
- (D) inductive effect

Sol.**Q.4** Alkyl halides react with dialkyl copper reagents to give

[AIEEE-2005]

- (A) alkyl copper halides
- (B) alkenes
- (C) alkenyl halides
- (D) alkanes

Sol.**Q.5**

Elimination of bromine from 2-bromobutane results in the formation of –

[AIEEE-2005]

- (A) predominantly 2-butene
- (B) equimolar mixture of 1 and 2-butene
- (C) predominantly 2-butyne
- (D) predominantly 1-butene

Sol.**Q.6**Among the following the one that gives positive iodoform upon reaction with I_2 and NaOH is –

[AIEEE 2006]

- (A) $C_6H_5CH_2CH_2OH$
- (B) $CH_3 - \overset{CH_3}{\underset{|}{CH}}CH_2OH$
- (C) $PhCHOHCH_3$
- (D) $CH_3CH_2CH(OH)CH_2CH_3$

Sol.**Q.7**Which of the following is the correct order of decreasing S_N^2 reactivity ?

[AIEEE 2007]

- (A) $RCH_2X > R_3CX > R_2CHX$
- (B) $RCH_2X > R_2CHX > R_3CX$
- (C) $R_3CX > R_2CHX > RCH_2X$
- (D) $R_2CHX > R_3CX > RCH_2X$
(X = a halogen)

Sol.

Q.8 The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is [AIEEE 2008]

(A) $(\text{CH}_3)_3\text{CCl}$ (B) $(\text{CH}_3)_2\text{CHCl}$
 (C) CH_3Cl (D) $(\text{C}_2\text{H}_5)_2\text{CHCl}$

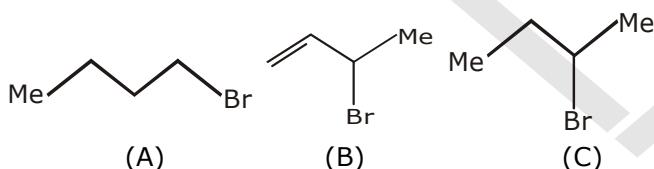
Sol.

Q.9 Which of the following on heating with aqueous KOH, produces acetaldehyde ?

[AIEEE 2009]

Sol.

Q.10 Consider the following bromides :



The correct order of SN1 reactivity is

[AIEEE 2010]

Sol.

11. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? [AIEEE 2012]

- (A) Isohexane
- (B) Neohexane
- (C) Tertiary butyl chloride.
- (D) Neopentane

Sol.

12. Iodoform can be prepared from all except :

- (A) 3 - Methyl - 2 - butanone
- (B) Isobutyl alcohol
- (C) Ethyl methyl ketone
- (D) Isopropyl alcohol

Sol.

13. What is DDT among the following

(A) Biodegradable pollutant
(B) Non-biodegradable pollutant
(C) Greenhouse gas
(D) A fertilizer

Sol.

LEVEL - II**JEE ADVANCED**

1. The ether

when treated with HI produces

[IIT 1999]

(A) (B)

(C) (D)

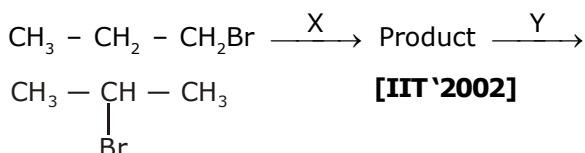
Sol.

2. The order of reactivity of the following alkyl halides for a SN^2 reaction is : [IIT 2000]

(A) RF > RCl > R-Br > R-I
 (B) R-F > R-Br > R-Cl > R-I
 (C) R-Cl > R-Br > RF > RI
 (D) R-I > RBr > R-Cl > R-F

Sol.

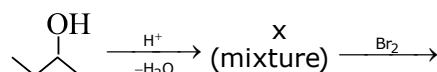
3 Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformation



(A) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
 (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
 (C) X = dilute aqueous NaOH, 20°C; Y = Br₂/CHCl₃, 0°C
 (D) X = concentrated alcoholic NaOH, 80°C; Y = Br₂/CHCl₃, 0°C

Sol.

4



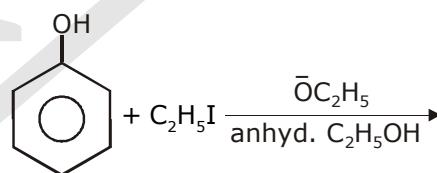
5 compounds of molecular formula C₄H₈Br₂
 Number of compounds in X will be:

[IIT 2003]

(A) 2 (B) 3
 (C) 4 (D) 5

Sol.

5.



[IIT 2003]

(A) C₆H₅OC₂H₅ (B) C₂H₅OC₂H₅
 (C) C₆H₅OC₆H₅ (D) C₆H₅I

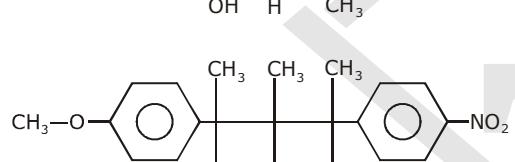
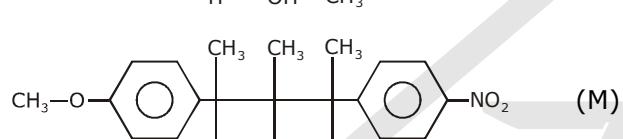
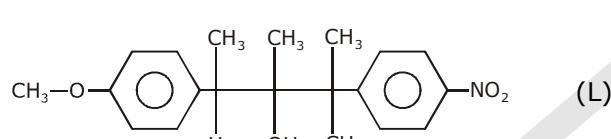
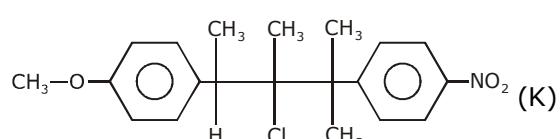
Sol.

6. Benzamide on treatment with POCl_3 gives
[IIT 2004]

(A) aniline (B) benzonitrile
(C) chlorobenzene (D) benzyl amine

Sol.

7. The following compound on hydrolysis in aqueous acetone will give : [IIT 2005]



(A) mixture of (K) and (L)
(B) mixture of (K) and (M)
(C) only (M) (D) Only (K)

Sol

8 Cyclohexene is best prepared from cyclohexanol by which of the following [IIT '2005]
 (A) conc. H_3PO_4 (B) conc. $HCl/ZnCl_2$
 (C) conc. HCl (D) Conc. HBr

Sol.

0

1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed?

(A) 

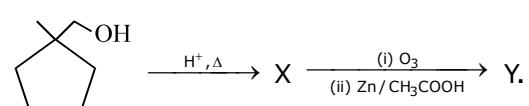
(B) 

(C) 

(D) 

Sol

10



Identify X and Y.

[IIT 2005]

Sol

11. Match the following :

[IIT 2006]

Column I

(A) $\text{CH}_3\text{—CHBr—CD}_3$ on treatment with alc. KOH gives $\text{CH}_2 = \text{CH—CD}_3$ as a major product

(B) Ph—CHBr—CH_3 reacts faster than Ph—CHBr—CD_3 .

(C) $\text{Ph—CH}_2\text{—CH}_2\text{Br}$ on treatment with $\text{C}_2\text{H}_5\text{OD}/\text{C}_2\text{H}_5\text{O}^-$ gives Ph—CD = CH_2 as the product.

(D) $\text{PhCH}_2\text{CH}_2\text{Br}$ and $\text{PhCD}_2\text{CH}_2\text{Br}$ react with same rate

Column II

(P) E1 reaction
KOH gives $\text{CH}_2 = \text{CH—CD}_3$ as a major product

(Q) E2 reaction

(R) E1 cb reaction gives Ph—CD = CH_2 as the product.

(S) First order reaction

Sol.

12. The reagent(s) for the following conversion.

[IIT 2007]



is/are

(A) alcoholic KOH

(B) alcoholic KOH followed by NaNH_2

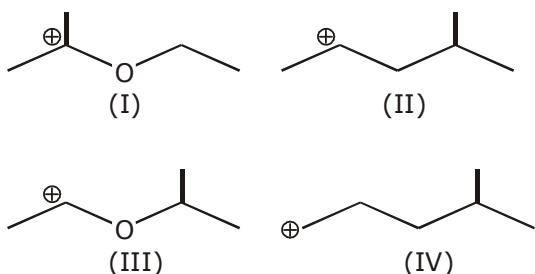
(C) aqueous KOH followed by NaNH_2

(D) $\text{Zn}/\text{CH}_3\text{OH}$

Sol.

15 The correct stability order for the following species is [IIT '2008]

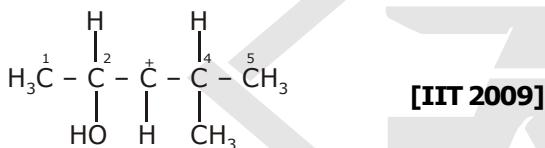
Sol.



(A) II > IV > I > III (B) I > II > III > IV
 (C) II > I > IV > III (D) I > III > II > IV

Sol.

16. In the following carbocation, H/CH₃ that is most likely to migrate positively charged carbon is



(A) CH_3 at C-4 (B) H at C-4
 (C) CH_3 at C-2 (D) H at C-2

Sol.

17. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are – **[IIT 2010]**

(A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$
 (D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$

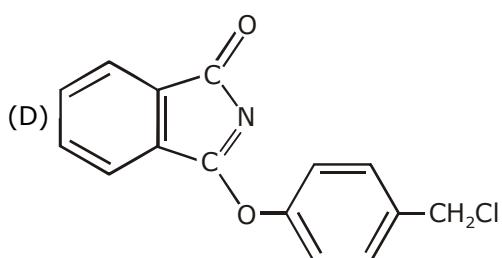
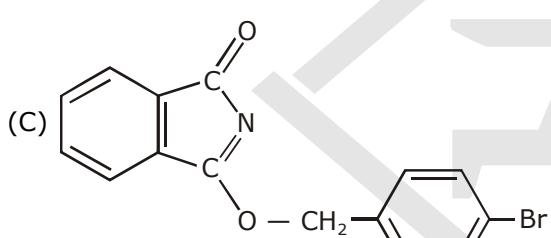
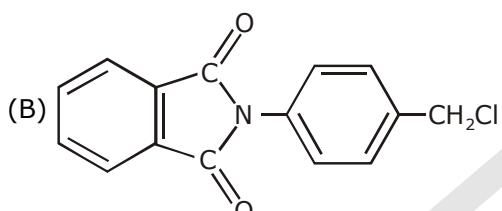
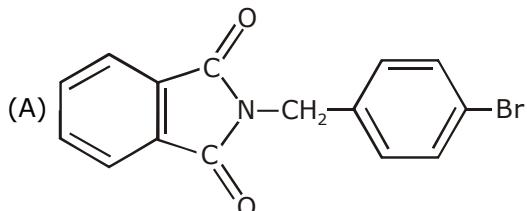
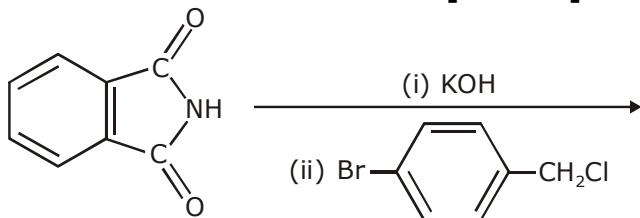
18

The bond energy (in kcal mol⁻¹) of a C - C single bond is approximately [IIT 2010]

Sol.

19. The major product of the following reaction is
:

[IIT 2011]

**Sol.****Subjective :**

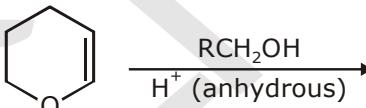
20. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is :

[IIT 2011]

Sol.

21. The major product of the following reaction is
:

[IIT 2011]

(A) a hemiacetal
(C) an ether(B) an acetal
(D) an ester**Sol.**

Answers

Answer Ex-I		JEE MAIN									
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1. B 2. B 3. B 4. C 5. C 6. C 7. C 8. C
 9. B 10. B 11. A 12. C 13. B 14. A 15. A 16. B
 17. A 18. A 19. B 20. B 21. A,B,D 22. A,B,C 23. B 24. C
 25. D 26. A 27. C 28. C 29. D 30. B 31. B
 32. C 33. A 34. B 35. D 36. C 37. A 38. B
 39. C

Answer Ex-II		JEE ADVANCED (OBJECTIVE)									
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1. A 2. C 3. A 4. C 5. B 6. A 7. D 8. A
 9. A 10. B 11. B 12. A 13. D 14. B 15. D 16. A
 17. A 18. D 19. B 20. B,D 21. A,B 22. B,C 23. A
 24. A 25. B 26. D 27. D 28. A
 29. A → S ; B → R ; C → Q ; D → P 30. A → T ; B → S ; C → R ; D → Q ; E → P
 31. A → P, Y ; B → Q, X ; C → R, W 32. A → S ; B → R ; C → Q ; D → P
 33. A → R ; B → Q ; C → P ; 34. A → P ; B → Q ; C → R ; D → S ; E → T
 35. A → S ; B → Q ; C → R ; D → P 36. A → 2 ; B → 1 ; C → 4 ; D → 3
 37. A → S ; B → R ; C → Q ; D → P 38. A → S ; B → Q ; C → P ; D → R
 39. B 40. A → W ; B → XY ; C → WY ; D → Z
 41. A → P ; B → Q, S ; C → Q, R ; D → R, S 42. A → P ; B → R ; C → Q ; D → T
 43. A → S ; B → R ; C → P ; D → S

S.NO.	SN1	SN2	BOTH
1		✓	
2			✓
3			✓
4	✓		
5		✓	
6		✓	
7			✓
8	✓		

44.

Answer Ex-III**JEE ADVANCED**

1. A	2. B	3. B	4. C	5. A	6. A	7. A	8. C
9. C	10. B	11. A	12. A	13. B	14. A	15. A	16. A
17. C	18. B	19. B	20. C	21. C	22. A	23. A	24. D
25. C	26. C	27. D	28. B	29. A	30. C	31. A	32. D
33. A	34. C	35. D	36. B	37. A	38. C	39. A	40. A
41. A	42. B	43. C					

Answer Ex-IV**PREVIOUS YEARS****LEVEL - I****JEE MAIN**

1. A	2. A	3. C	4. D	5. A	6. C	7. B	8. C
9. D	10. A	11. D	12. B	13. B			

LEVEL - II**JEE ADVANCED**

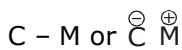
1. A,D	2. D	3. B	4. B	5. A	6. B	7. A	8. A
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9. D	10. (x) 	(y) $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{(CH}_2\text{)}_4\text{-CHO}$	11. A→Q; B→Q; C→R,S, ; D→P,S,				
12. B	13. A	14. A	s15. D	16. D	17. D	18. C	19. A
20. 0.005	21. B						

GRIGNARD REAGENT

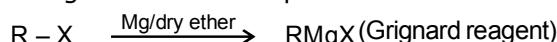
1.1 Organometallic compounds

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond. For example

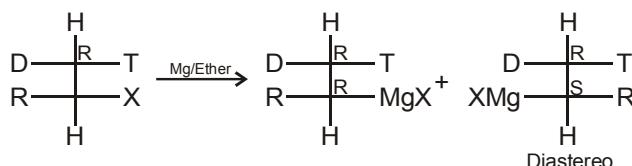
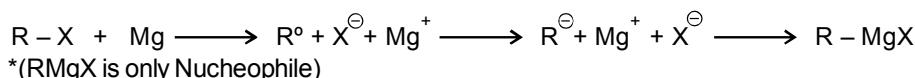


(Where C is a carbon atom of an organic molecule and M is a metal atom)

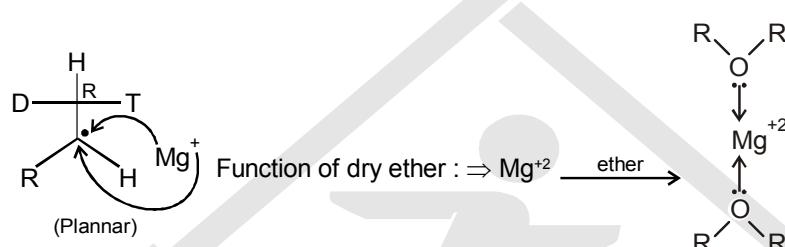
If the metal atom is attached to oxygen, nitrogen, sulphur, etc. then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.



Mechanism

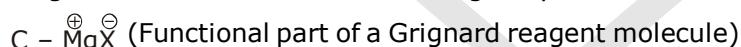


Reason



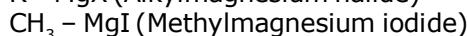
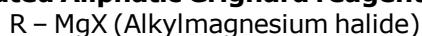
Note : It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

Most important examples of organometallic compounds are Grignard reagents. In Grignard reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.



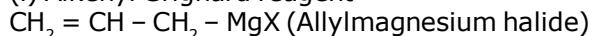
In organometallic compounds, the metal atom can be bonded to carbon of a hydrocarbon radical (Saturated, unsaturated, aliphatic, alicyclic or aromatic) or carbon atom of a heterocyclic radical. Some examples are given below.

1. Saturated Aliphatic Grignard reagent

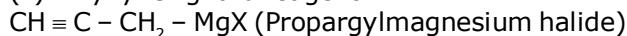


2. Unsaturated Aliphatic Grignard reagent

(i) Alkenyl Grignard reagent



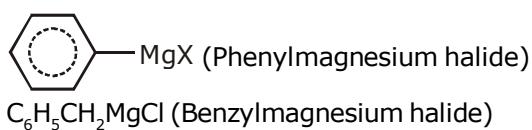
(ii) Alkynyl Grignard reagent



3. Alicyclic Grignard reagent



4. Aromatic Grignard reagent



5. Heterocyclic Aromatic Grignard reagent

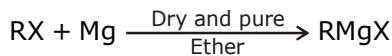


6. Heterocyclic Nonaromatic Grignard reagent

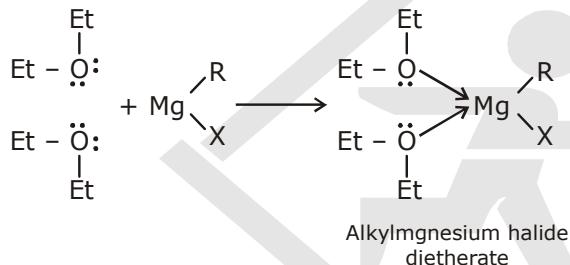


In a Grignard reagent, X is generally Cl, Br or I (Halogen). Order of reactivity is as follows:
 $\text{RMgI} > \text{RMgBr} > \text{RMgCl}$

1.2 Preparation



Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard reagent by completing the octet on magnesium atom.



1.3 Reactivity of grignard reagents.

It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of grignard reagent. Therefore, there is a tendency of forming carbonion by heterolysis of this polar coordinate bond as follows.



The carbanion (a nucleophile) formed as shown above, attacks the positively charged electrophilic centre of other compound. Therefore, it can be said that if a Grignard reagent is regarded as the substrate, then electrophilic displacement (ESR) reaction takes place.

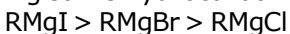


If Grignard reagent is regarded as the attacking reagent, then the nucleophilic carbonion of Grignard reagent will attack on the other compound taken as substrate.



1.4 Reactions of Grignard reagent

On having same hydrocarbon radical, the order of reactivity of Grignard reagents will be as follows:

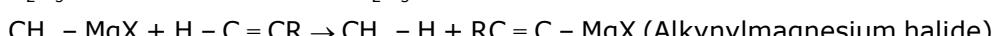
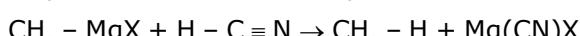
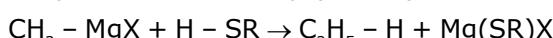
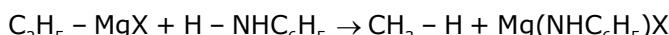
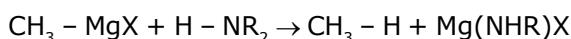
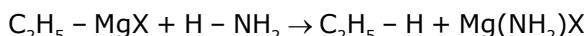
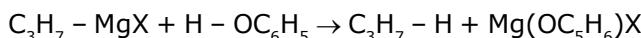
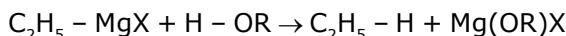
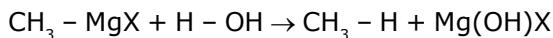
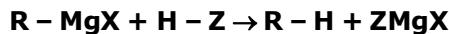


Grignard reagent gives the following two type of reactions.

- (i) Acid base reaction
- (ii) electrophilic-nucleophilic reaction

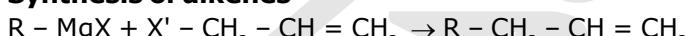
1.5 1. Synthesis of Alkanes

(i) With compounds having reactive hydrogen atom



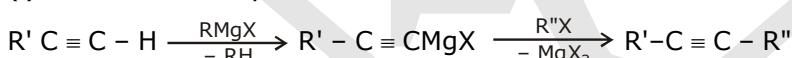
Methane gas is released on reacting methylmagnesium iodide with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called **Zerewitinoff method of estimation of reactive hydrogen atoms.**

2. Synthesis of alkenes

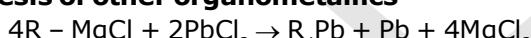


3. Synthesis of higher alkynes

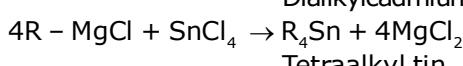
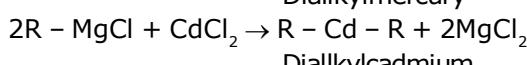
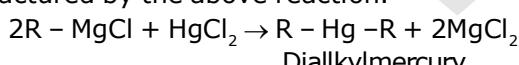
(i) Non-terminal alkynes



4. Synthesis of other organometallics



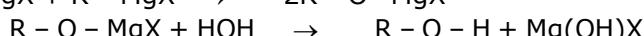
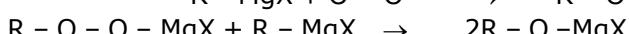
Two important antiknock compounds, tetraethyllead (T. E. L.) and tetramethyllead (T. M.L.) are manufactured by the above reaction.



5. Synthesis of Alcohols

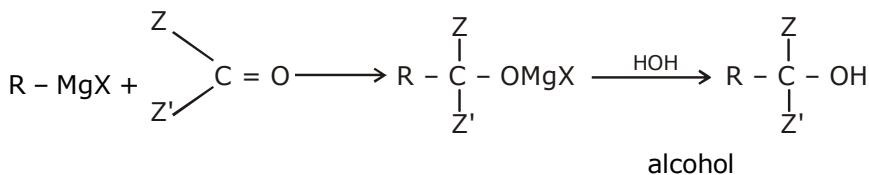
There are following methods to obtain alcohols from Grignard reagent.

(i) From Oxygen



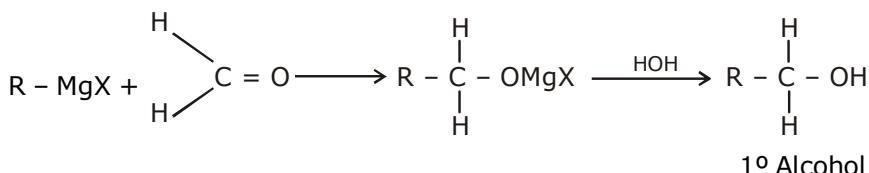
Primary, secondary and tertiary alcohols can be obtained by above reaction.

(ii) From Carbonyl compounds



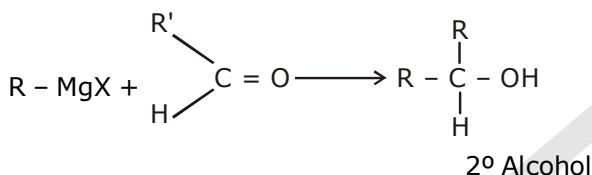
(a) Primary or 1° Alcohols

Primary alcohols are formed on taking formaldehyde



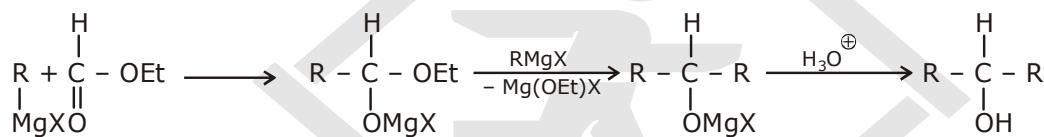
(b) Secondary or 2° alcohols

(1) From RCHO Secondary alcohols are formed of any aldehyde other than formaldehyde.



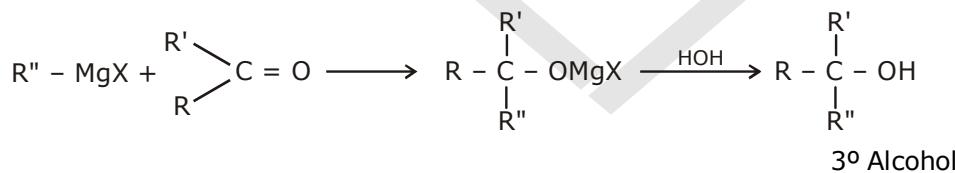
(2) From formic ester:

Secondary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and adding formic ester to it.

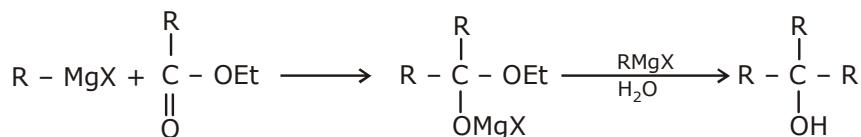


(c) Tertiary or 3° alcohols

(1) Tertiary alcohols are formed by taking any ketone



(2) Tertiary alcohols are also obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester of a higher homologue of formic acid.

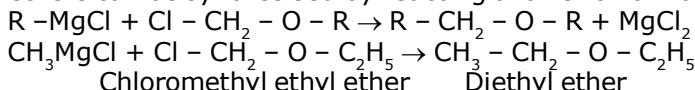


Various alcohols can be prepared by changing R in the above synthesis.

6.

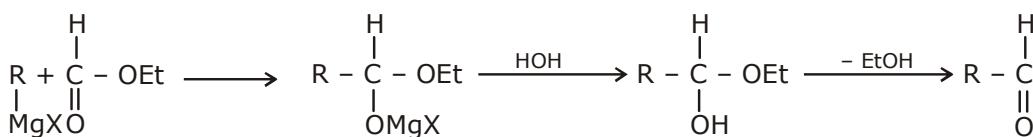
Synthesis of Ethers

Higher ethers can be synthesised by reacting a lower chlorinated ether with Grignard reagent.



7. Synthesis of Aldehydes

Corresponding aldehyde is obtained on hydrolysis of the product obtained by reacting of formic ester and Grignard reagent in equimolecular ratio.

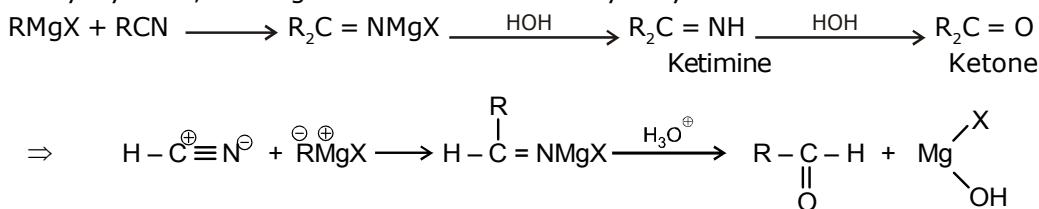


The above conversion can be simplified as follows for convenience.

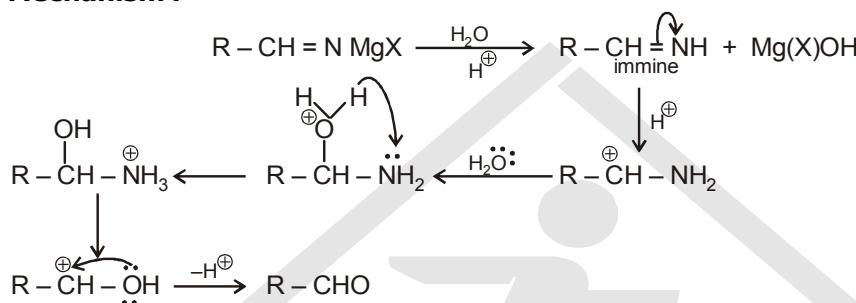
8. Synthesis of Ketones

(i) From Alkyl cyanides

A ketimine is formed on hydrolysis of the adduct obtained by the reaction of Grignard reagent and an alkyl cyanide, which gives ketone on further hydrolysis.

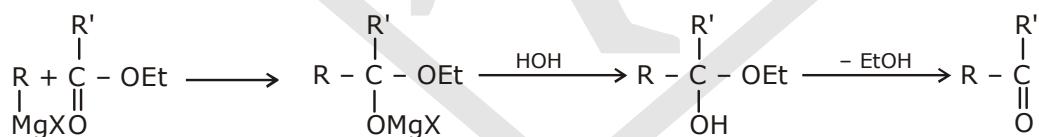


Mechanism :

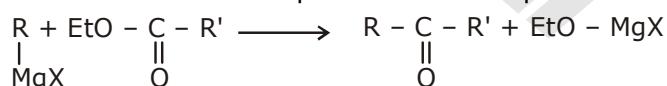


(ii) From carboxylic esters (other than formic ester)

(ii) From carboxylic esters (other than formic ester)
Ketone is formed on taking R' in place of H of formic ester.

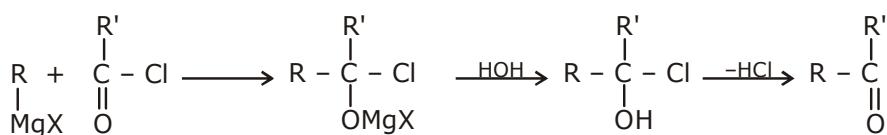


The above reaction sequence can be simplified as follows for convenience.



(iii) From carboxylic acid chlorides

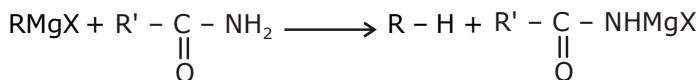
Formyl chloride is unstable. Therefore, acetyl chloride is regarded as the first member of this family.



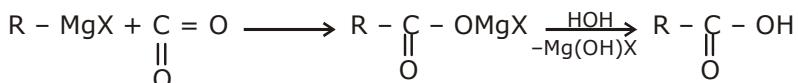
or



(iv) From carboxylic acid amides

**9. Synthesis of carboxylic acids**

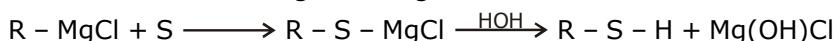
A carboxylic acid is formed on hydrolysis of the adduct formed by passing carbon dioxide in the ethereal solution of a Grignard reagent.

**10. Synthesis of carboxylic acid esters**

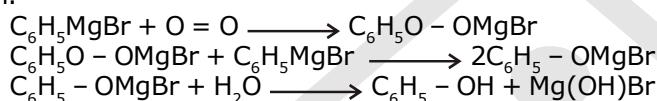
Higher esters are formed on reacting the chlorinated ester of lower carboxylic acid with grignard reagent.

**11. Synthesis of mercaptans**

Alkanethiols, i.e. mercaptan is formed on hydrolysis of the product obtained by adding sulphur to the ethereal solution of Grignard reagent.

**12. Synthesis of phenols**

Phenol is obtained on hydrolysis of the product obtained by reaction of arylmagnesium bromide with oxygen.

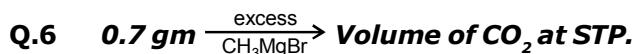
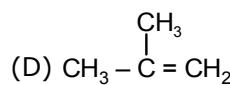
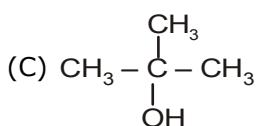
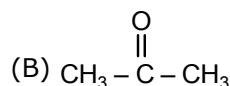
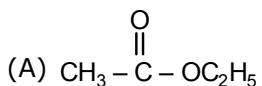
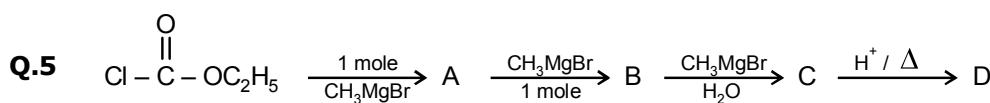
**PRACTICE PROBLEM**

Q. 1 Which of the following compound reacts with methylmagnesium iodide to form n-Butane?
 (A) n -Butyl alcohol (B) n - Propyl alcohol (C) Isopropyl iodide (d) n - Propyl chloride

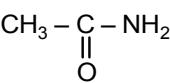
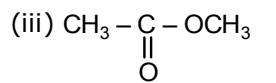
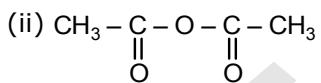
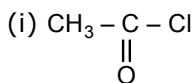
Q. 2 Which of the following reactions forms an unsaturated Grignard reagent?
 (A) RMgX + C₂H₂ (B) RMgX + CH₃C ≡ CCH₃
 (C) HC ≡ CNa + RMgCl (D) RMgX + CH₂ = CHCl

Q. 3 Which of the following compound is formed on hydrolysis of the product obtained on the reaction of ethylmagnesium iodide and propanone?
 (A) tert-Amyl alcohol (B) Isoamyl alcohol
 (C) tert-Butyl alcohol (D) Isobutyl alcohol

Q. 4 The compound formed on hydrolysis of the adduct of methylmagnesium iodide and benzaldehyde
 (A) Is a phenol (B) Gives iodoform test
 (C) Is a primary alcohol (D) Gives benzophenone on oxidation



Q.7 Compare the reactivity of the above derivative with grignard reagent (Nu^\ominus).



ANSWER

1. D

2. A

3. A

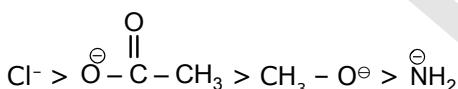
4. B

5. C

6. $\frac{0.7}{M_w} \times 2 \times 22.4 \Rightarrow \text{volume of CH}_4$

7. All acid derivative gives NSR

a > b > c > d Reason extent of the positive charge at $\text{C}=\text{O}$ or leaving group.



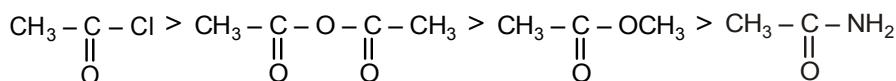
poor Base

HCl > CH₃COOH > CH₃OH > NH₃

most ceridic

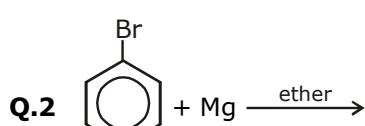
weaker the conjugate base bast the leaving group.

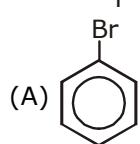
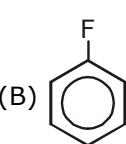
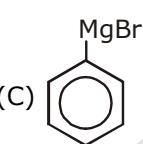
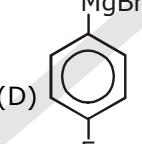
Reactivity with Nu^\ominus



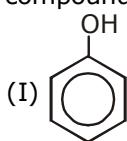
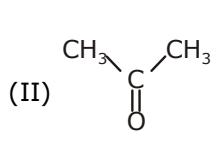
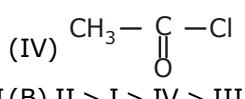
EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)****Q.1** $C_6H_5COOH + CH_3MgI \rightarrow ?$

(A) $C_6H_5COOMgI$
 (B) CH_4
 (C) Both A & B
 (D) None

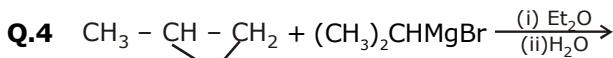
Sol.

(A) 
 (B) 
 (C) 
 (D) 

Sol.**Q.3** The reactivity order of CH_3MgBr with the following compounds is:

(I) 
 (II) 
 (III) $CH_3 - Cl$
 (IV) 

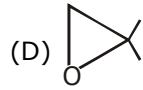
(A) I > IV > II > III (B) II > I > IV > III
 (C) I > II > IV > III (D) IV > II > I > III

Sol.

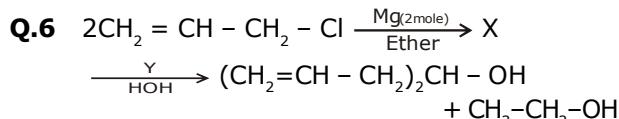
(A) $CH_3 - (CH_2)_4 - CH_2 - OH$
 (B) $CH_3 - CH = CH - CH - CH_3$
 $\quad\quad\quad |$
 $\quad\quad\quad CH_3$
 (C) $CH_3 - CH - CH_2 - CH - CH_3$
 $\quad\quad\quad |$
 $\quad\quad\quad CH_3$
 (D) $CH_3 - CH - CH_2 - CH_3$
 $\quad\quad\quad |$
 $\quad\quad\quad CH(CH_3)_2$

Sol.

Product
What is the product

(A) $HO - CH_2 - C - CH_3$
 $\quad\quad\quad |$
 $\quad\quad\quad OH$
 (B) $Cl - CH_2 - C - OEt$
 $\quad\quad\quad |$
 $\quad\quad\quad OH$
 (C) $CH_3 - CH_2 - C - OEt$
 $\quad\quad\quad ||$
 $\quad\quad\quad O$
 (D) 

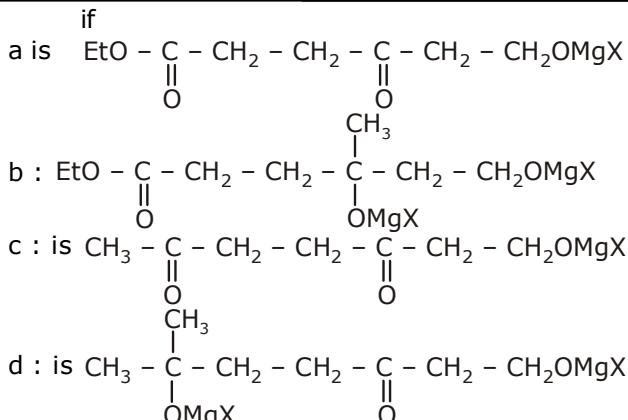
Sol.



In the above chemical reaction, Y may be

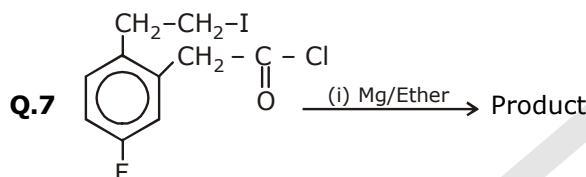
- (A) Ethyl formate
- (B) Methyl formate
- (C) Isopropyl methanoate
- (D) Ethanoylchloride

Sol.

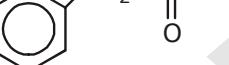


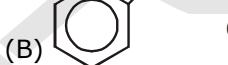
Which is incorrect

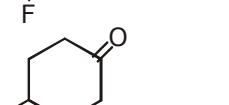
Sol.

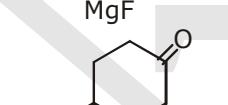


The final product of the reaction is

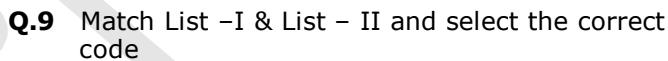
(A) 

(B) 

(C) 

(D) 

Sol.



List – I

(a) $\text{RMgX} + \text{HCHO} \rightarrow \text{adduct} \xrightarrow{\text{H}_3\text{O}^+}$
n-carbon

(b) $\text{RMgX} + (\text{CH}_2)_2\text{O} \rightarrow \text{adduct} \xrightarrow{\text{H}_3\text{O}^+}$
n-carbon

(c) $\text{RMgX} + \text{CO}_2 \rightarrow \text{adduct} \xrightarrow{\text{H}_3\text{O}^+}$
n-carbon

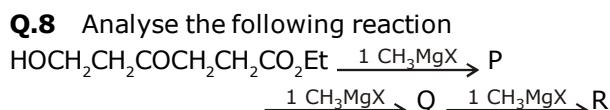
(d) $\text{RMgX} + \text{Ph-C}\equiv\text{N} \rightarrow \text{adduct} \xrightarrow{\text{H}_3\text{O}^+}$
n-carbon

List – II

- (i) Ketone
- (ii) 1° Alcohol ($n+1$) carbon
- (iii) acid ($n+1$) carbon
- (iv) 1° Alcohol ($n+2$) carbon

Code	i	ii	iii	iv
A	a	d	b	c
B	d	a	c	b
C	d	b	a	c
D	b	a	c	d

Sol.



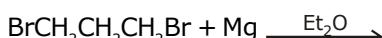
Q.10 Match List - I & List - II and select the correct code

List - I	List - II
(a) RMgI + Acetonitrile ($\text{CH}_3\text{C}\equiv\text{N}$)	(i) Alkanone
(b) RMgI + carbon disulphide	(ii) Ester
(c) RMgI + Ethyl chloroformate	(iii) 1°Alcohol
(d) RMgI + Oxirane	(iv) Dithionic acid

Code	i	ii	iii	iv
A	c	b	a	d
B	a	d	b	c
C	c	d	b	a
D	a	c	d	b

Sol.

Q.12 The reaction



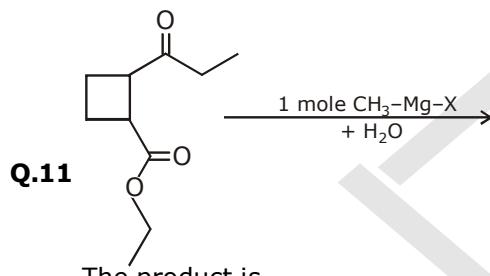
(A) $\text{CH}_3\text{CH}_2\text{CH}_3$ (B) $\text{BrMgCH}_2\text{CH}_2\text{CH}_2\text{MgBr}$
 (C)  (D) $\text{CH}_3\text{CH}=\text{CH}_2$

Sol.

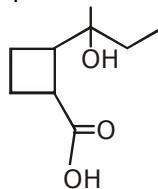
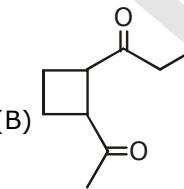
Q.13 The order of reactivity of alkyl halide in the reaction $\text{R-X} + \text{Mg} \longrightarrow \text{RMgX}$ is

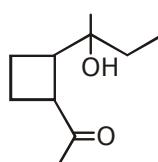
(A) $\text{RI} > \text{RBr} > \text{RCI}$ (B) $\text{RCI} > \text{RBr} > \text{RI}$
 (C) $\text{RBr} > \text{RCI} > \text{RI}$ (D) $\text{RBr} > \text{RI} > \text{RCI}$

Sol.



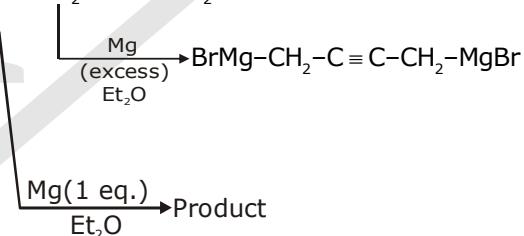
The product is

(A)  (B) 

(C)  (D) All of these

Sol.

Q.14 $\text{Br}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{Br}$



The major product is :

(A) $\text{Br}-\text{Mg}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{Br}$
 (B) Cyclobutyne
 (C) $-(\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2)_n$
 (D) $\text{CH}_2=\text{C}\equiv\text{C}=\text{CH}_2$

Sol.

Q.15 One conversion into Grignard followed by treatment with ethanol, how many alkyl halides (excluding stereoisomers) would yield 2-methyl butane.

(A) 2 (B) 3 (C) 4 (D) 5

Sol.

Q.16 How many litres of methane would be produced when 0.595 g of CH_3MgBr is treated with excess of $\text{C}_4\text{H}_9\text{NH}_2$

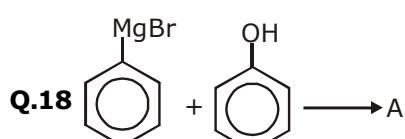
(A) 0.8 litre (B) 0.08 litre
(C) 0.112 litre (D) 1.12 litre

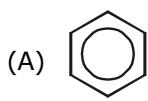
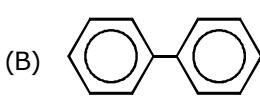
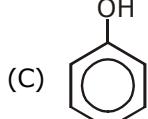
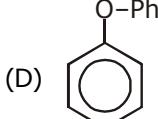
Sol.

Q.17 How many litres of ethene would be produced when 2.62 g of vinyl magnesium bromide is treated with 224 ml of ethyne at STP.

(A) 0.224 litre (B) 0.08 litre
(C) 0.448 litre (D) 1.12 litre

Sol.

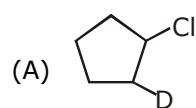
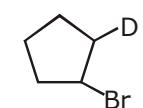


(A)  (B) 
(C)  (D) 

Sol.



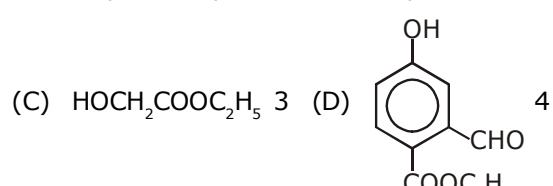
is

(A)  (B) 
(C)  (D) None of these

Sol.

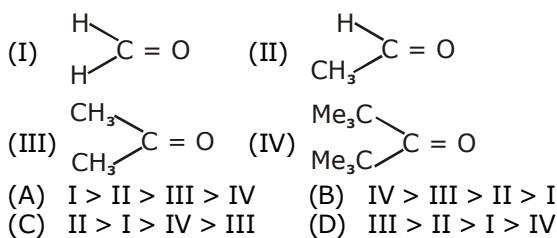
Q.20 Compounds are shown with the no. of RMgX required for complete reaction, select the incorrect option

(A) $\text{CH}_3\text{COOC}_2\text{H}_5$ 1 (B) CH_3COCl 2



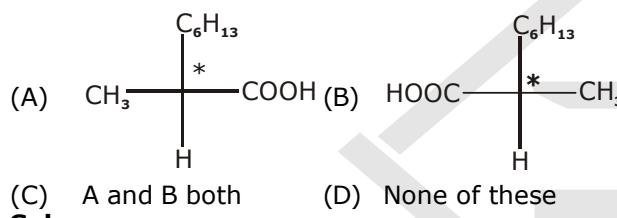
Sol.

Q.21 What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent



Sol.

Q.22 (R) - 2-Bromoocetane $\xrightarrow{\begin{array}{l} \text{(i) Mg} \\ \text{(ii) CO}_2 \\ \text{(iii) H}^+ \end{array}}$ X is



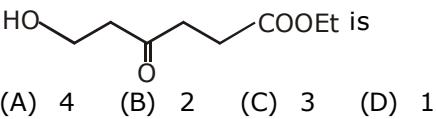
Sol.

Q.23 In which one of the following reaction products are not correctly matched in

- (A) $\text{RMgX} + \text{CO}_2 \xrightarrow[2\text{H}^+]{}$ Carboxylic acid
- (B) $\text{RMgX} + \text{C}_2\text{H}_5\text{OH} \longrightarrow$ Alkane
- (C) $\text{RMgX} + \text{CH}_3\text{CH}_2\text{Cl} \longrightarrow$ Alkene
- (D) $\text{RMgX} + \text{Cl}-\text{CH}_2-\text{O}-\text{CH}_2-\text{Cl} \longrightarrow$ Ether

Sol.

Q.24 The number of moles of grignard reagent consumed per mole of the compound

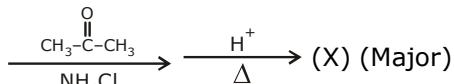
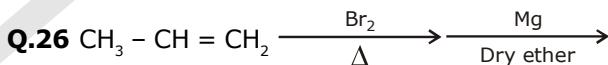


Sol.

Q.25 Select the correct statement :

- (A) 1,4-dibromobutane react with excess of magnesium in ether to generate di-Grignard reagent.
- (B) 1,2-dichlorocyclohexane treated with G.R and dont give cyclo alkene.
- (C) Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg.
- (D) 1,3-dichloropropane by treatment with Zn dust or Mg forms cyclopropane.

Sol.

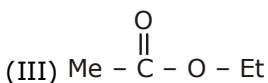


End product of above reaction is :

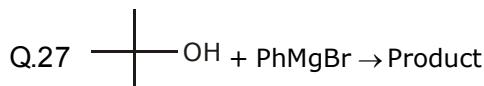
- (A) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \overset{\text{CH}_2}{\underset{\text{||}}{\text{C}}} - \text{CH}_3$
- (B) $\text{CH}_2 = \text{CH} - \text{CH} = \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$
- (C) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$
- (D) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{OH}$

Sol.

Q.29 Order of rate of reaction of following compound with phenyl magnesium bromide is:

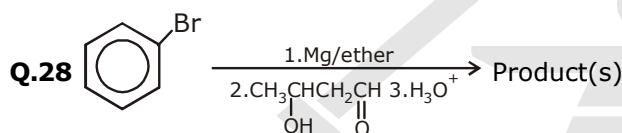


(A) I > II > III (B) II > III > I
 (C) III > I > II (D) II > I > III

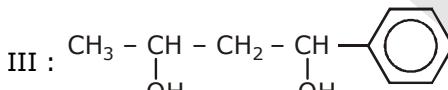
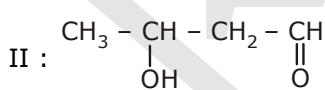
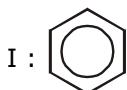
Sol.

Product is :

(A) Ter. Butane (B) Methoxy benzene
 (C) Benzene (D) Phenol

Sol.

Select the product from the following

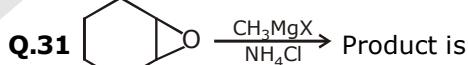


(A) III (B) I, III (C) I, II (D) II, III

Sol.

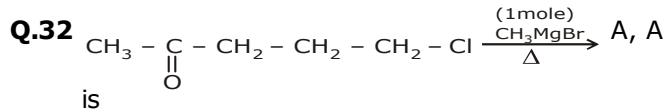
Q.30 Select the correct order of decreasing reactivity of the following compounds towards the attack of Grignard reagent

(I) Methyl benzoate (II) Benzaldehyde
 (III) Benzoylchloride (IV) Acetophenone
 (A) II > III > I > IV (B) I > II > III > IV
 (C) III > II > IV > I (D) II > IV > I > III

Sol.

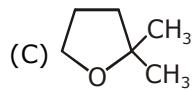
(A) Enantiomer (B) Diastereoisomer
 (C) Meso (D) Achiral

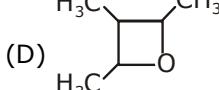
Sol.



(A) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$

(B) $\text{CH}_3 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

(C) 

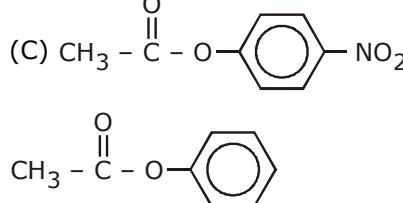
(D) 

Sol.

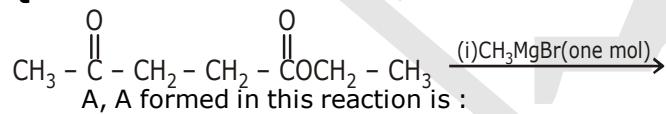
Q.34 Select the correct order of reactivity towards Grignard reagent for nucleophilic attack.

(A) $\text{R} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{O} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{R} < \text{R} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{H}$

(B) $\text{Cl} - \text{CH}_2 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{H} > \text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{H}$

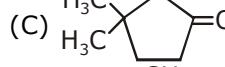
(C) $\text{CH}_3 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{O} - \text{C}_6\text{H}_4 - \text{NO}_2 <$


(D) $\text{R} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{OR} > \text{R} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{NH}_2$

Sol.**Q.33**

(A) $\text{CH}_3 - \overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\Delta}{\text{C}}} - \text{COCH}_2 - \text{CH}_3$

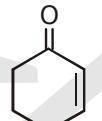
(B) $\text{CH}_3 - \overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\Delta}{\text{C}}} - \text{CH}_3$

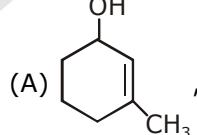
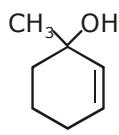
(C) 

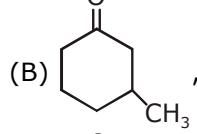
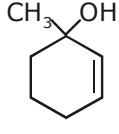
(D) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}} - \text{CH}_3$

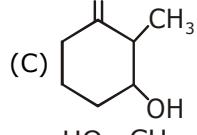
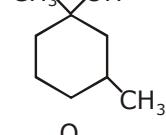
Sol.

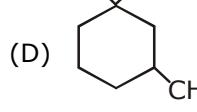
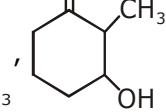
Q.35 In the reaction sequence:

 $\xrightarrow[\text{(ii) H}_2\text{O}/\text{H}^+]{\text{(i) CH}_3\text{MgBr/CuCl}} \text{(X) Major + (Y)}$
(X) & (Y) respectively

(A)  , 

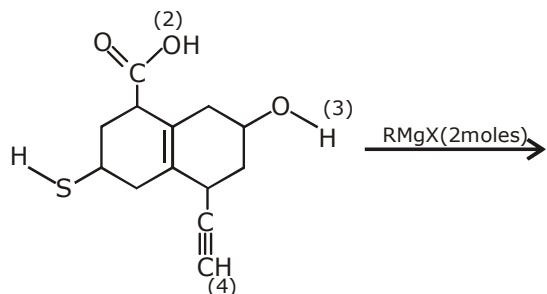
(B)  , 

(C)  , 

(D)  , 

Sol.

Q.36



Deprotonation will occur from the following positions:

Sol.

Q.38 Which of the following is incorrect

(A) $\text{Cl}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5 \xrightarrow[\text{(1eq)}]{\text{CH}_3\text{MgX}} \text{CH}_3-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$

(B) $\text{CH}_3-\underset{\substack{\text{OC}_2\text{H}_5 \\ \diagup \\ \diagdown}}{\text{C}}-\text{OC}_2\text{H}_5 \xrightarrow[\text{(1eq)}]{\text{C}_2\text{H}_5\text{MgX}} \text{CH}_3-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$

(C) $\text{CH}_3\text{MgX} + \text{C}(=\text{S})=\text{S} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3-\text{C}(=\text{S})-\text{SH}$

(D) $\text{CH}_3\text{MgX} + \text{C}(=\text{O})=\text{O} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3-\text{C}(=\text{O})-\text{OH}$

Sol.

Q.39 Which reaction gives 1° aromatic amine as major product.

(A)  $\xrightarrow{\text{Mg/ether}}$ $\xrightarrow{\text{NH}_3}$

(B)  $\xrightarrow{\text{Mg/ether}}$ $\xrightarrow{\text{NH}_3}$

(C)  $\xrightarrow{\text{Mg/ether}}$ $\xrightarrow{\text{NH}_3}$

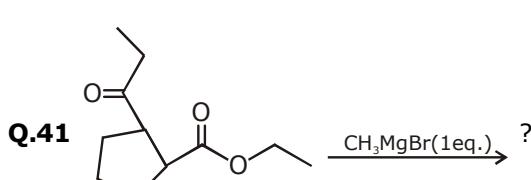
(D)  $\xrightarrow{\text{Hg(OAc)}_2}$ $\xrightarrow{\text{NH}_3/\text{NaBH}_4}$

Sol.

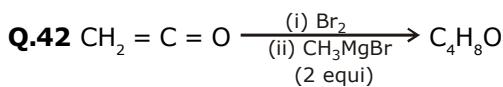
Sol.

Q.40 $\text{CH}_3\text{MgBr} + \text{CH}_2 = \text{CH} - \overset{\text{O}}{\underset{||}{\text{C}}} - \text{H} \xrightarrow{\text{H}_3\text{O}^+}$
Product (1,4 addition). It is

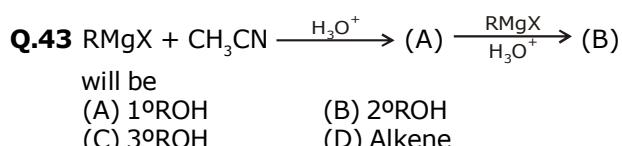
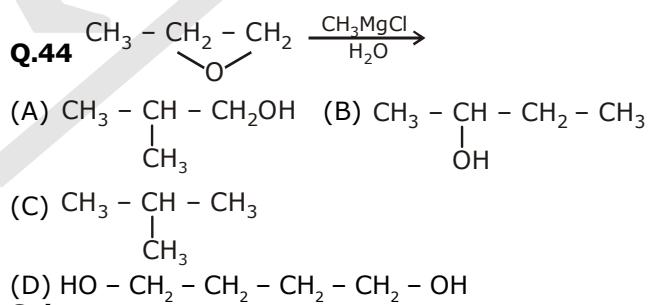
(A) $\text{CH}_2 = \text{CH} - \begin{matrix} \text{OH} \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{matrix} - \text{H}$ (B) $\text{CH}_2 - \begin{matrix} \text{CH} = \text{CH} \\ | \\ \text{OH} \end{matrix} - \text{CH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (D) None

Sol.

(A) (B) (C) (D)

Sol.

(A) (B) (C) (D) All of these

Sol.**Sol.****Sol.**

(A) (B) (C) (D) All of these

Q.45 The reaction of 1 mole each of p-hydroxy acetophenone and methyl magnesium iodide will give

(A) $\text{CH}_4 + \text{IMgO} \longrightarrow \text{C}_6\text{H}_5\text{COCH}_3$

(B) $\text{CH}_3 - \text{O} - \text{C}_6\text{H}_5 - \text{COCH}_3$

(C) $\text{CH}_3 - \overset{\text{OMgI}}{\underset{\text{CH}_3}{\text{C}}} - \text{C}_6\text{H}_5 - \text{OH}$

(D) $\text{CH}_3\text{O} - \text{C}_6\text{H}_5 - \text{COCH}_3$

Sol.**Sol.**

Q.48 Consider the given organometallic compound.

(I) $(\text{CH}_3)_2\text{Hg}$ (II) $(\text{CH}_3)_2\text{Zn}$
 (III) $(\text{CH}_3)_2\text{Mg}$ (IV) CH_3Li

The correct decreasing order of ionic character is
 (A) I > II > III > IV (B) II > I > III > IV
 (C) I > III > II > IV (D) IV > III > II > I

Sol.

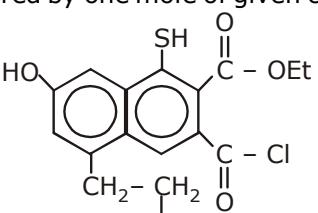
Q.46 (i)  + $\text{PhMgBr} \xrightarrow{r_1} \text{PhCH}_2\text{CH}_2\text{OH}$

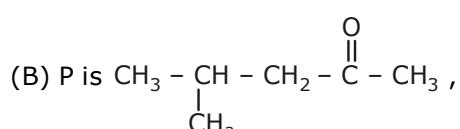
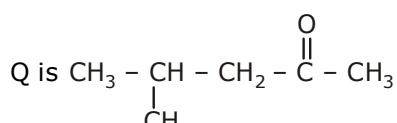
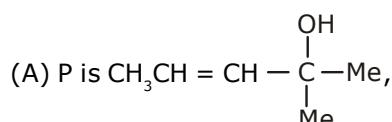
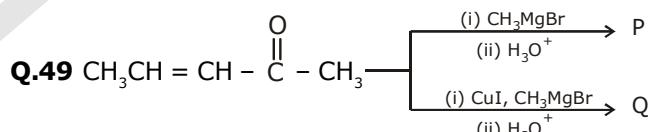
(ii)  + $\text{PhMgBr} \xrightarrow{r_2} \text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH}$

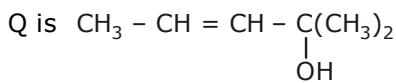
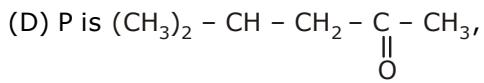
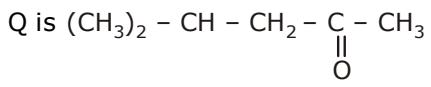
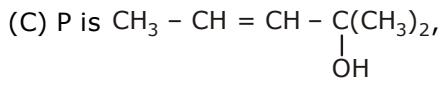
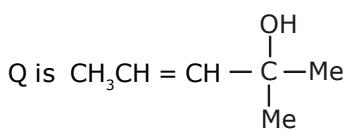
(A) $r_2 > r_1$ (B) $r_1 > r_2$
 (C) $r_1 = r_2$ (D) $r_1 = 2r_2$

Sol.

Q.47 How many moles of Grignard reagent will be required by one mole of given compound?


 (A) 7 (B) 6 (C) 8 (D) 5





Sol.

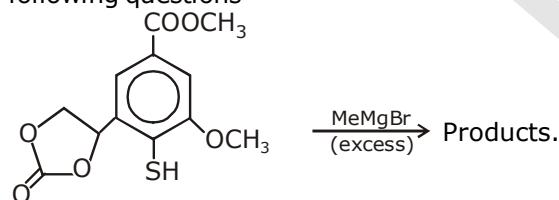
Q.51 How many product will be formed in given reaction (excluding stereo)

(A) 2 (B) 3 (C) 4 (D) 5

Sol.

For Q. No. 50 to Q. No. 52

Consider the given reaction and answer the following questions



Q.50 No. of RMgX consumed in the reaction is
 (A) 4 (B) 5 (C) 6 (D) 7

Sol.

Q.52 Which of the following reaction will give the same Hydrocarbon formed as one of the product in the above reaction.

(A) $\text{EtMgBr} + \text{Me-OH} \rightarrow$
 (B) $\text{PhMgBr} + \text{Me-OH} \rightarrow$
 (C) $\text{MeMgBr} + \text{Ph-OH} \rightarrow$
 (D) $\text{MeMgBr} + \text{CH}_3\text{-CHO} \rightarrow$

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

More than one option may correct

Q.1 $\text{RX} + \text{Mg} \xrightarrow{\text{Ether}} \text{RMgX} \xrightarrow{\text{CH}_3\text{OH}} \text{n-Butane}$
 What can be R in the above reaction sequence ?
 (A) n-Butyl (B) sec-Butyl
 (C) n-Propyl (D) Isopropyl

Sol.

Q.2 Which of the following compounds formed by the reaction sec-butylmagnesium iodide with a terminal alkyne
 (A) Isobutane (B) n-Butane
 (C) Higher alkyne (D) Unsaturated Grignard's reagent

Sol.

Q.3 n-Propyl alcohol is obtained on hydrolysis of the adduct obtained by the reaction of
 (A) EtMgX and HCHO
 (B) MeMgX and $(\text{CH}_2)_2\text{O}$
 (C) EtMgX and O_2
 (D) MeMgX and (CH_3CHO)

Sol.

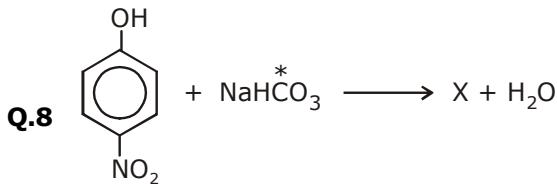
Q.4 A tertiary alcohol  can be prepared by grignard reagent and
 (A) O_2 (B) Epoxide
 (C) Ketone (D) Acid derivatives specially acid halide

Sol.

Q.5 3-Phenyl-3-pentanol can be prepared from a Grignard reagent and other component which can be
 (A) 3-Pentanone (B) Ethyl benzoate
 (C) Ethyl phenyl ketone (D) Propanoyl chloride

Sol.

Q.6 Which of the following have to be reacted and the product hydrolysed for obtaining the simplest chiral alkanol
 (A) $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{MgBr}$
 (B) $\text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{MgBr}$
 (C) $\text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{MgI}$
 (D) $\text{CH}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{MgCl}$

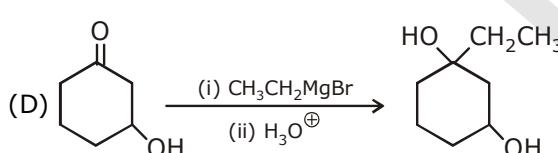
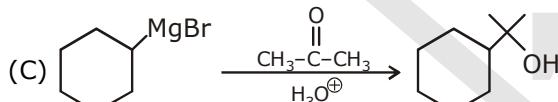
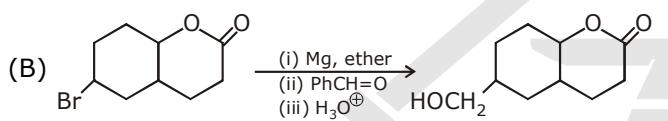
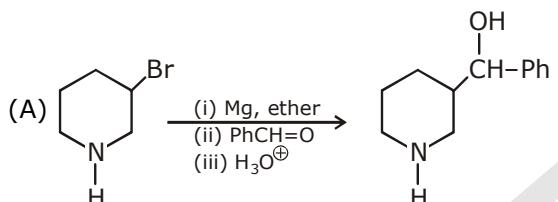
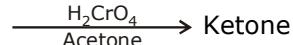
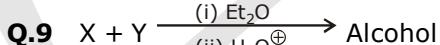
Sol.

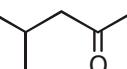
Which of the following statement is correct

- (A) Z' can give CO_2 gas with BaCO_3
- (B) Z , on reaction with propyne gives ethene
- (C) Z can show substitution reaction and addition reaction
- (D) All are incorrect

Sol.

Q.7 Point out the following incorrect Grignard synthesis.

**Sol.**

Ketone is  if X is Grignard reagent, then

- (A) X can be isobutyl metanesulfonate



- (B) Y can be $\text{CH}_3-\text{CH}-\text{CH}=\text{O}$



- (C) Y can be $\text{CH}_3-\text{CH}-\text{COCl}$

- (D) X can be isopropyl magnesium iodide

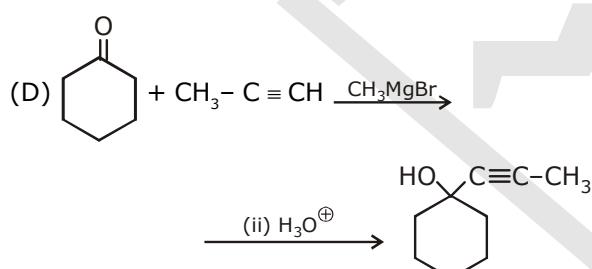
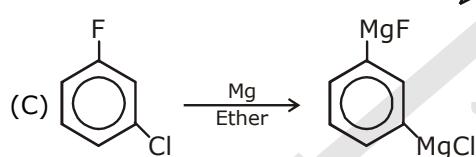
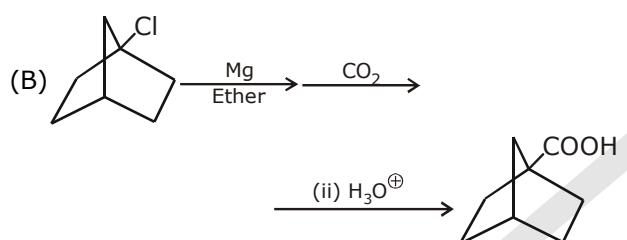
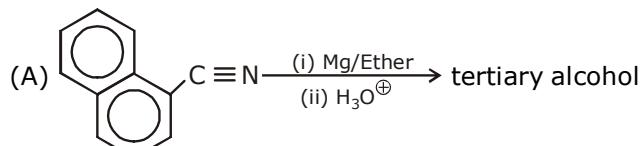
Sol.

Q.11 Which of the following reacts with Grignard reagent to give alkane?

(A) nitro ethane (B) acetyl acetone
(C) acetaldehyde (D) acetone

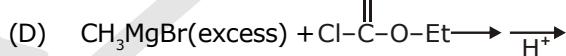
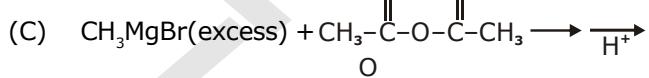
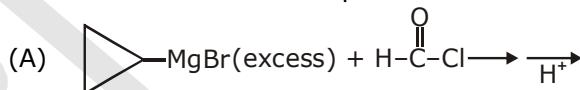
Sol.

Q.10 Which reaction is/are correct

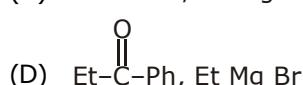
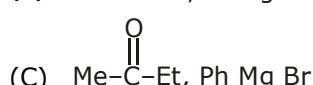
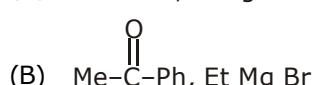
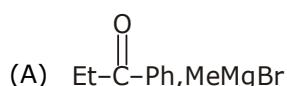
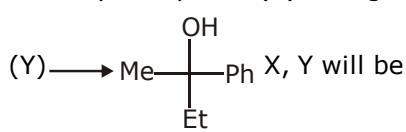


Sol.

Q.12 In which of the following reactions 3° alcohol will be obtained as a product.

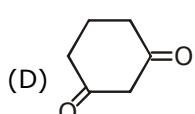
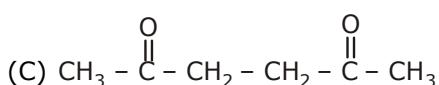
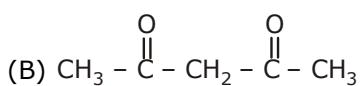
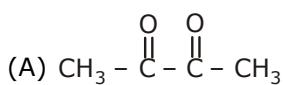
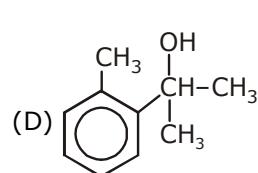
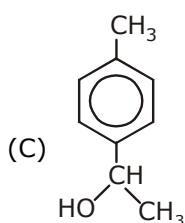
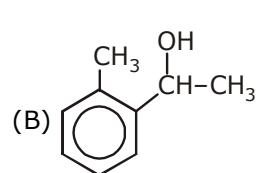
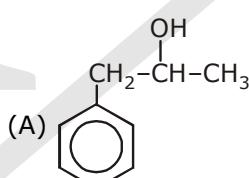


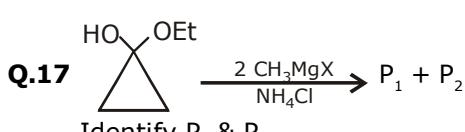
Sol.

GRIGNARD REAGENT**Q.13** Carbonyl compound (X) + Grignard reagent**Sol.****Q.14** $\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OC}_2\text{H}_5 \xrightarrow{2\text{CH}_3\text{MgBr}}$ A. Product

A formed

(A) Is ethyl acetate

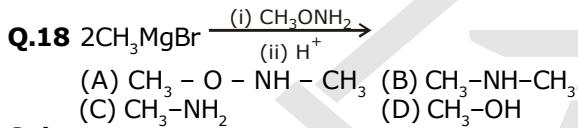
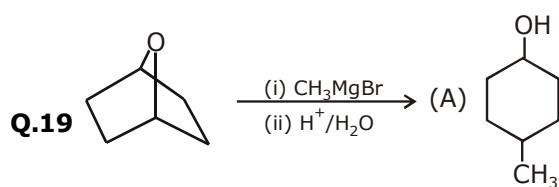
(B) Further react with $\text{CH}_3\text{MgBr}/\text{H}_3\text{O}^+$ to give acetone(C) Further react with $\text{CH}_3\text{MgBr}/\text{H}_3\text{O}^+$ to give t-butyl alcohol(D) Can give pinacol when treated with Mg followed by H_2O **Sol.****Q.15** Nucleophilic addition of Grignard reagent cannot occur in**Sol.****Q.16** $\text{PhCH}_3 \xrightarrow[\text{(C)}]{\text{Cl}_2, \text{h}\nu} (\text{A}) \xrightarrow[\text{(B)}]{\text{Mg, ether}} (\text{B}) \xrightarrow[\text{(D)}]{\text{CH}_3\text{CHO, NH}_4\text{Cl}}$ **Sol.**

Identify P₁ & P₂

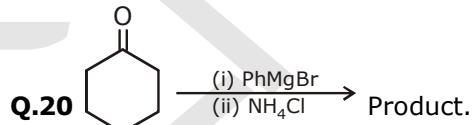
(A) CH_4 (B)

(C)

(D)

Sol.**Sol.**

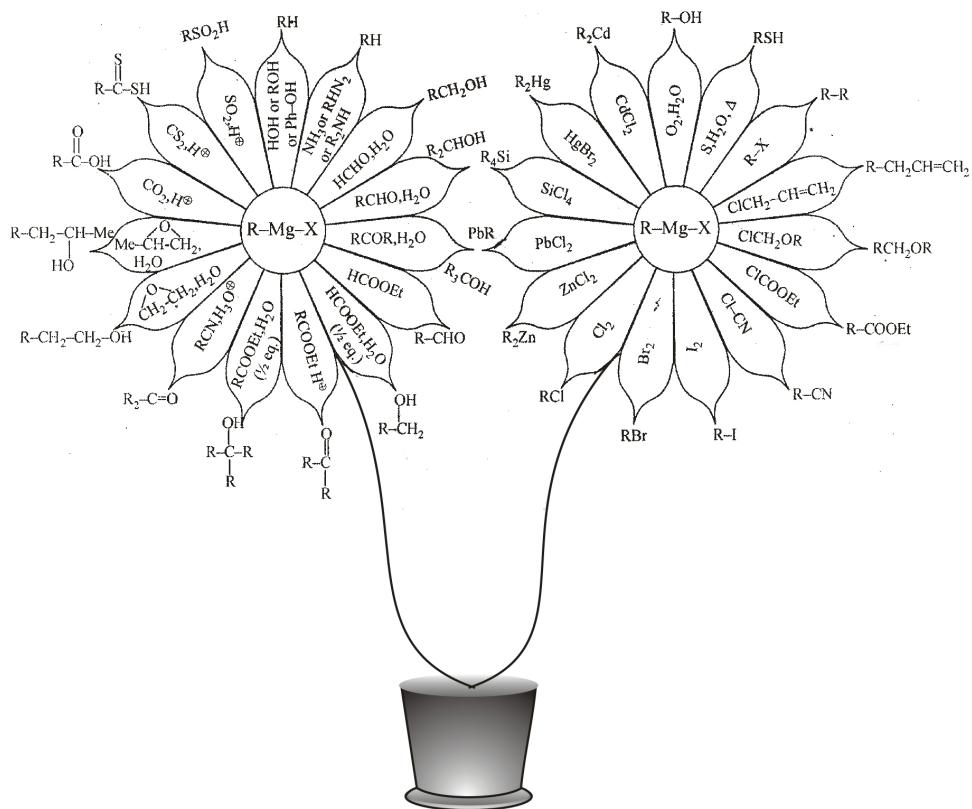
(A) The product is optically active
 (B) The product contains plane of symmetry
 (C) The product shows geometrical isomerism
 (D) The product shows optical isomerism

Sol.

Products in this reaction will be
 (A) Stereoisomers (B) Enantiomer
 (C) Diastereomers (D) Geometrical isomers

Sol.

General reaction of G. R.



ANSWER-KEY

Exercise-I

Q.1 C

Q.2 D

Q.3 A

Q. 4 C

Q.5 D

Q.6 A

Q.7 D

Q.8 B

Q.9 B

Q.10 D

Q.11 A

Q.12 C

Q.13 A

Q.14 D

Q.15 C

Q.16 C

Q.17 C

Q.18 A

Q.19 D

Q.20 A

Q.21 A**Q.22** C**Q.23** C**Q.24** A**Q.25** A,D**Q.26** B**Q.27** C**Q.28** C**Q.29** A**Q.30** C**Q.31** A**Q.32** C**Q.33** C**Q.34** B**Q.35** B**Q.36** A**Q.37** C**Q.38** B**Q.39** B**Q.40** C**Q.41** D**Q.42** A**Q.43** C**Q.44** B**Q.45** A**Q.46** B**Q.47** A**Q.48** D**Q.49** C**Q.50** C**Q.51** C**Q.52** C

Exercise-II

Q.1 AB**Q.2** BD**Q.3** AB**Q.4** ABCD**Q.5** ABC**Q.6** BC**Q.7** ABD**Q.8** ABC**Q.9** ABD**Q.10** D**Q.11** AB**Q.12** BCD**Q.13** ABC**Q.14** CD**Q.15** BD**Q.16** ABC**Q.17** AB**Q.18** CD**Q.19** BC**Q.20** ACD